Transitioning Research in the Physical Sciences to Planetary Science

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Structure & Chemistry

- Imaging laser-induced breakdown
- Atomic force microscopy + IR
- Electron-induced X-ray spectroscopy
- Fluorescence & Raman

Volatiles & gases

- Molecular absorption spectroscopy

Lab-on-a-chip systems

- Capillary electrophoresis
- Force-detected NMR

Emerging astrobiology instruments

One approach for life detection—look for structure & chemistry

Macroscopic --------------- Microscopic ----------------- "nanoscopic"

<u>Find the structures</u>

<u>Determine their chemistry</u>

Elemental composition

Chirality

Complex organic molecules

Isotopic fractionation

µCE with MOD

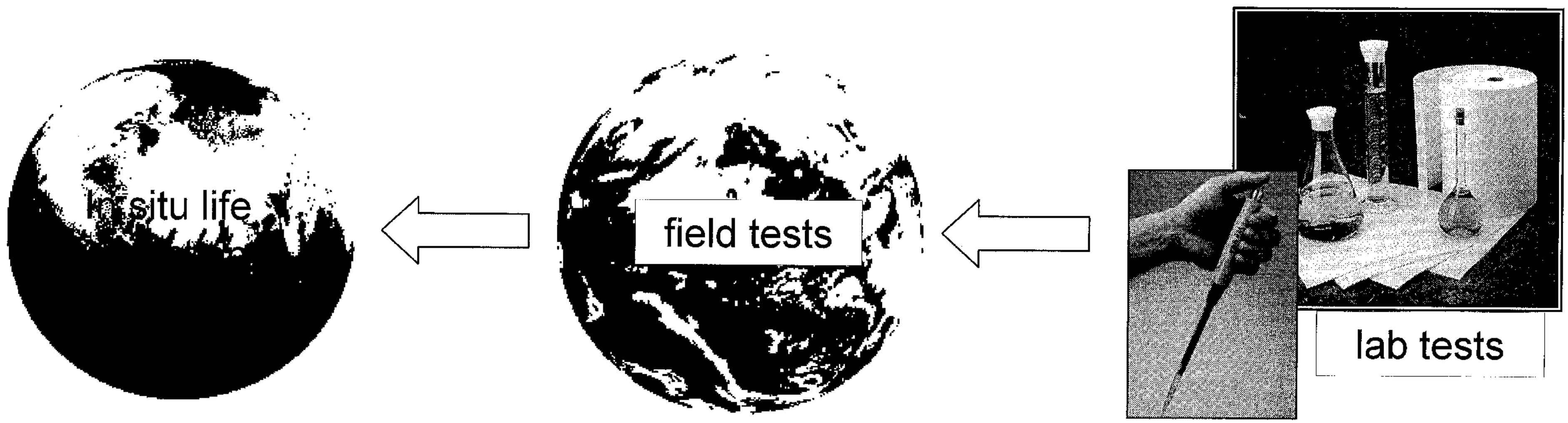
Imaging probe with LIBS

AFM with IR spectroscopies

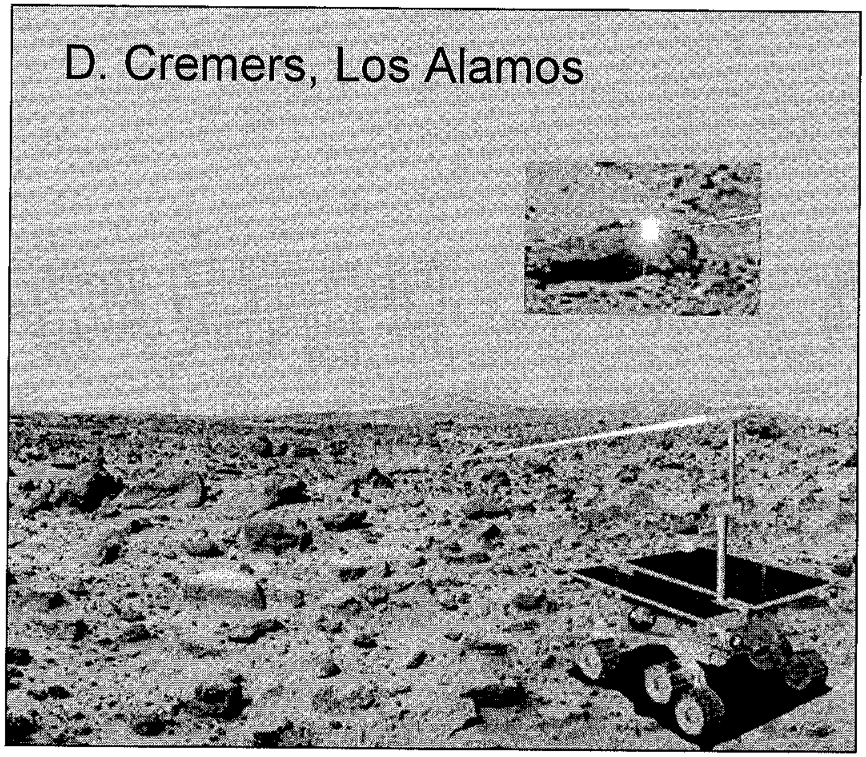
UV Raman + fluorescence

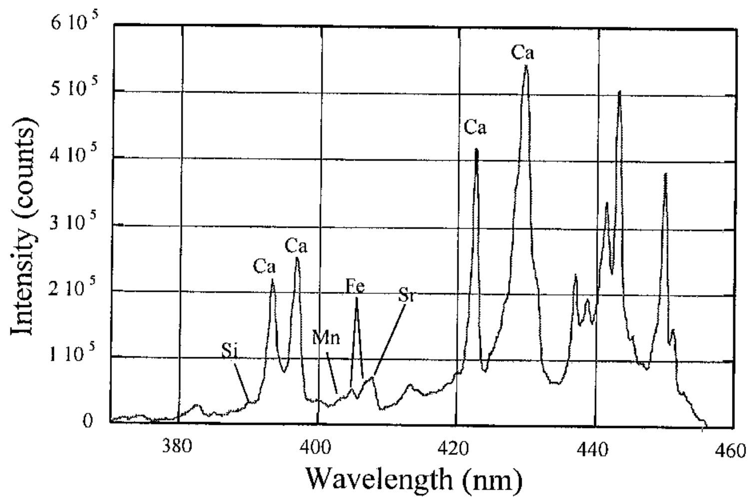
FD-NMR

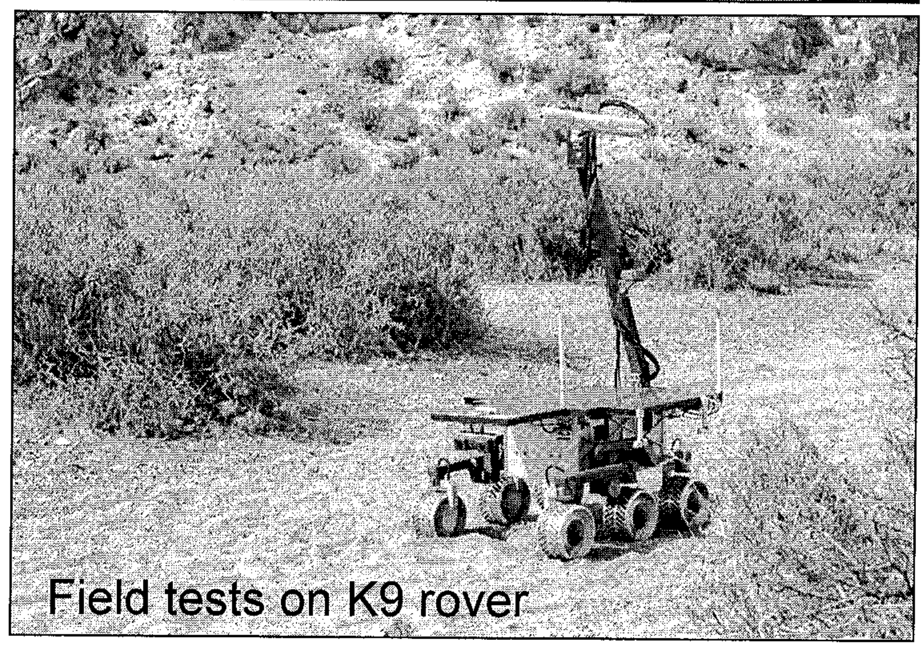
TDL absorption spectroscopy



LIBS for "remote" analysis


D. Cremers, Los Alamos

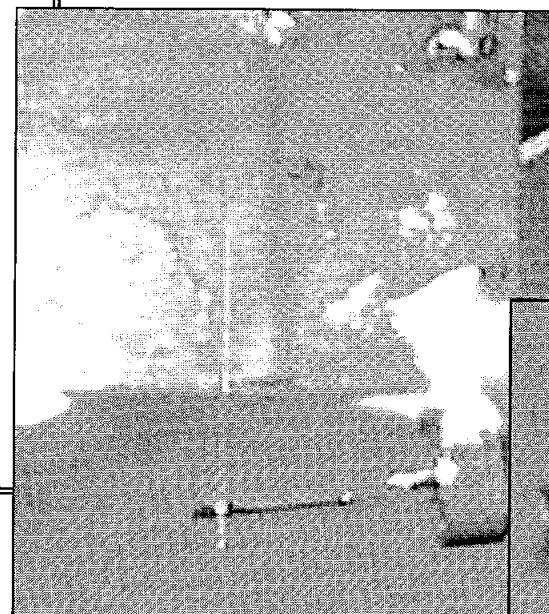


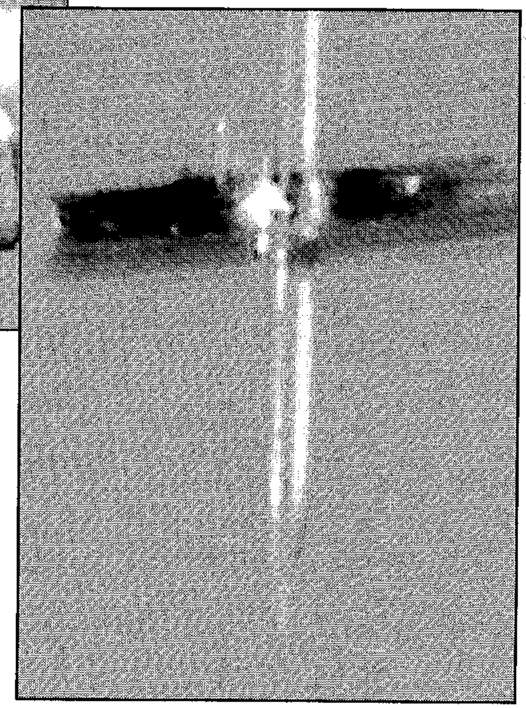

Field tests on K9 rover

In-situ LIBS-based chemical imager

Dmitri Kossakovski
J. Kirschvink, Caltech

QuickTime™ and a
decompressor
are needed to see this picture.

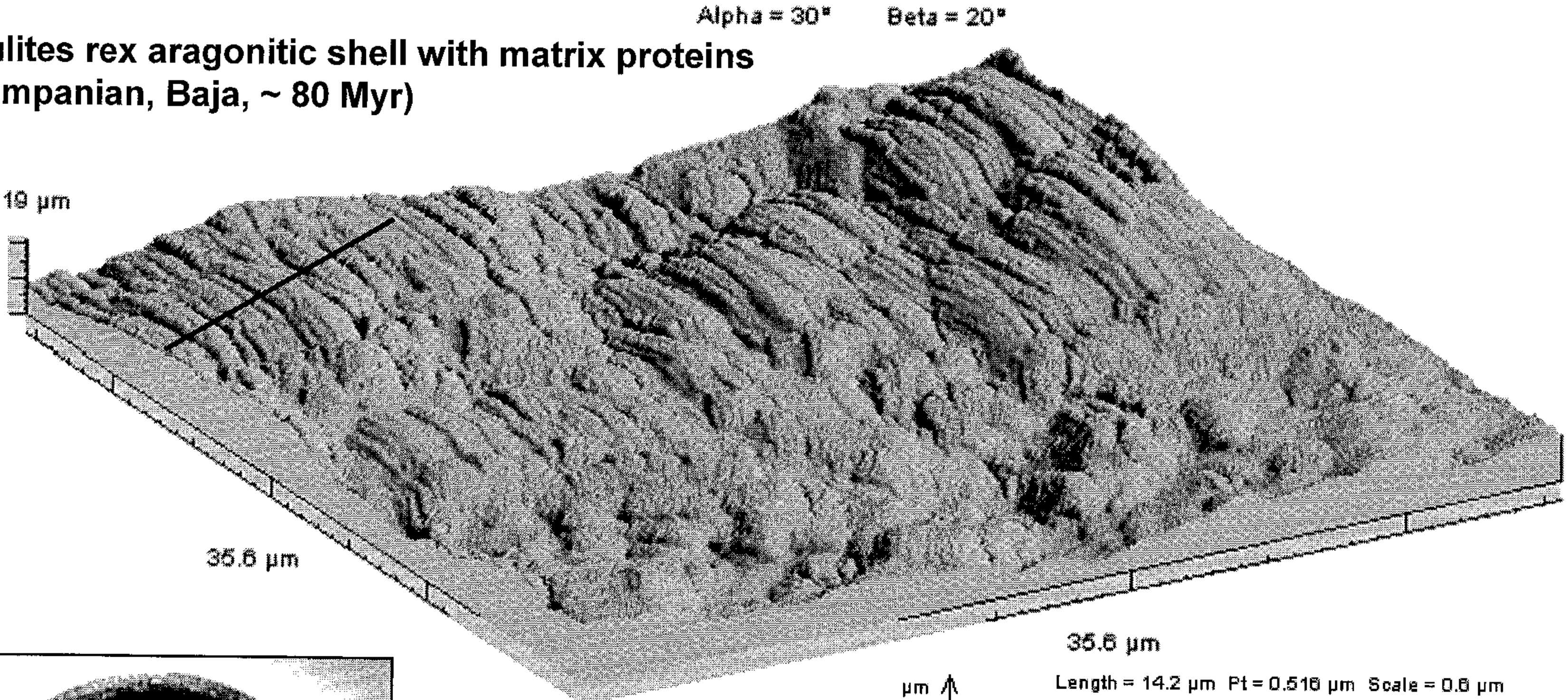


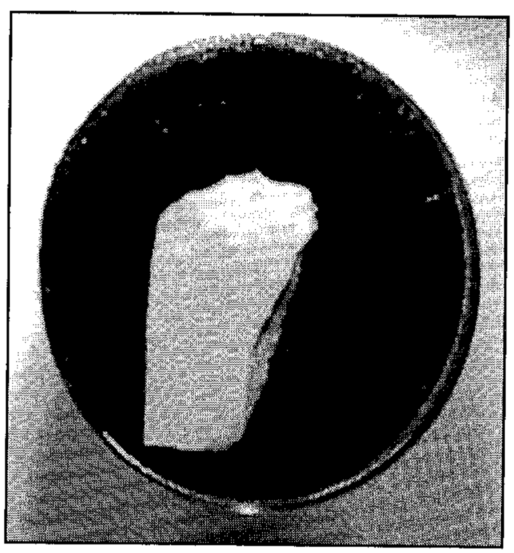


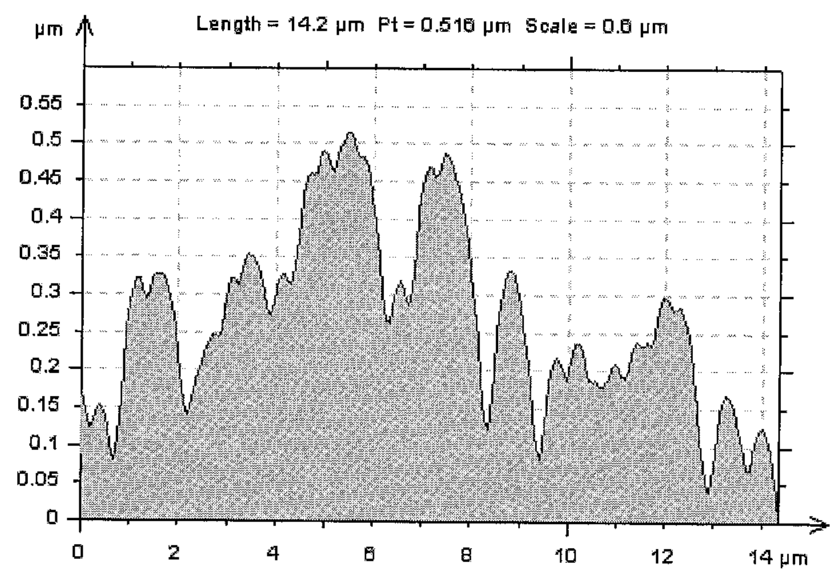
- **Scanning probe microscopy coupled with laser-induced breakdown spectroscopy**
  - **Topographic imaging**
  - **Elemental analysis registered to the topgraphy**

Topographic imaging

Bacculites rex aragonitic shell with matrix proteins (U. Campanian, Baja, ~ 80 Myr)

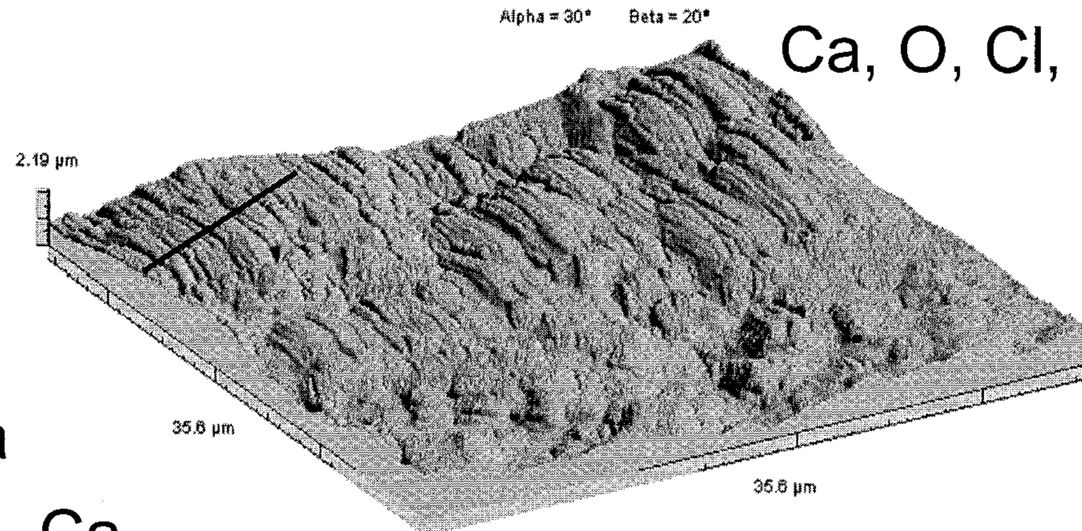


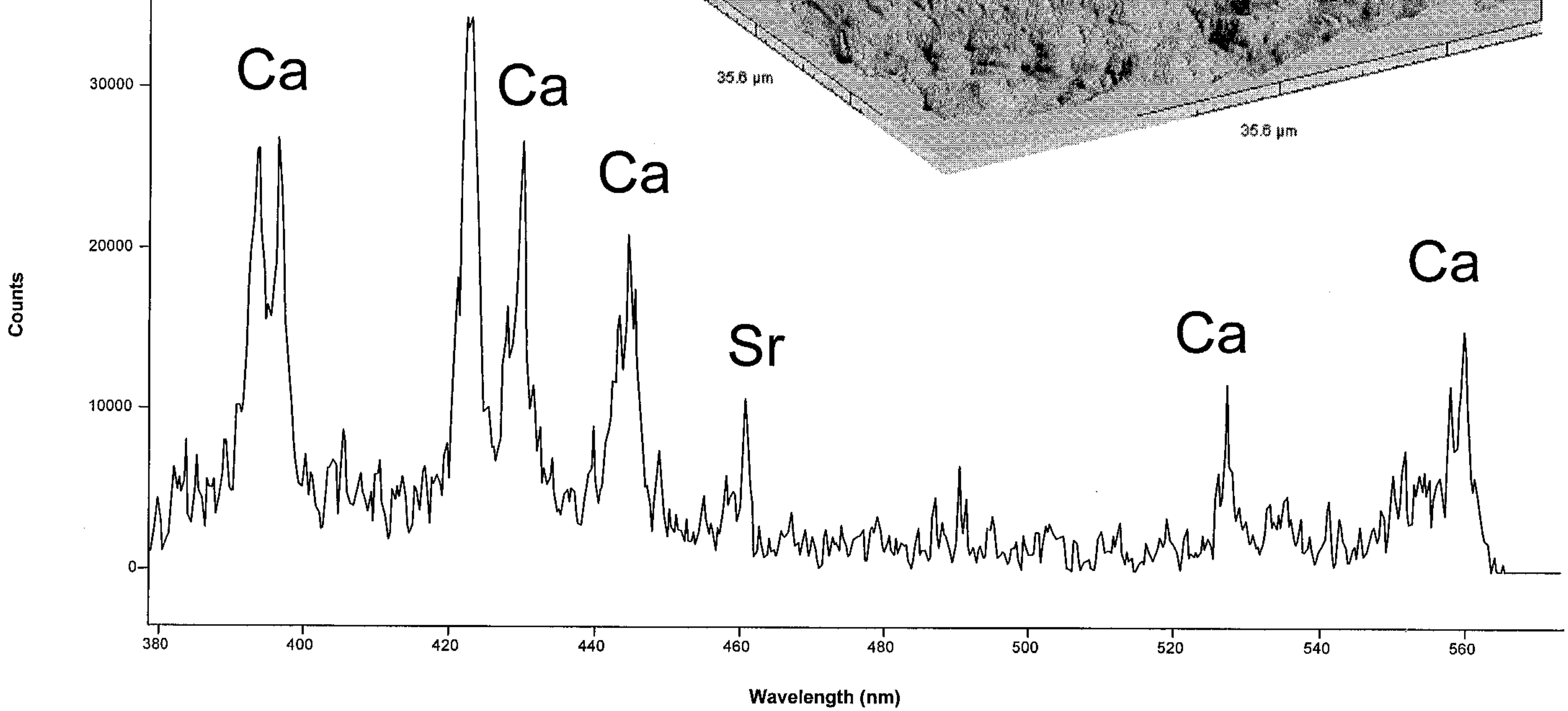




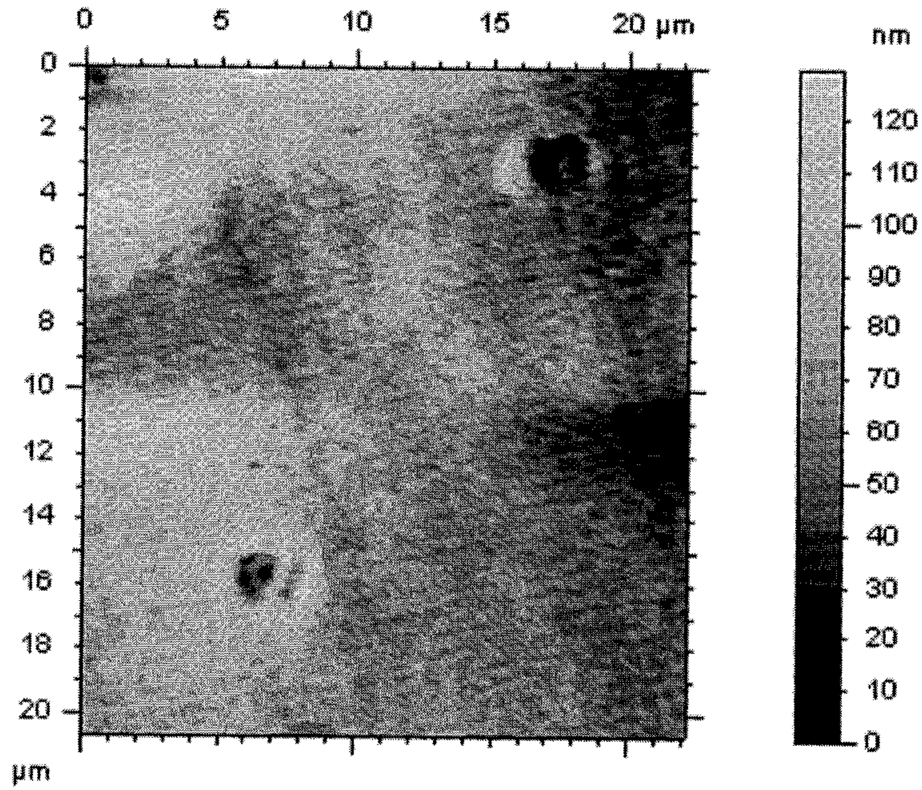
LIBS spectrum of fossil shell

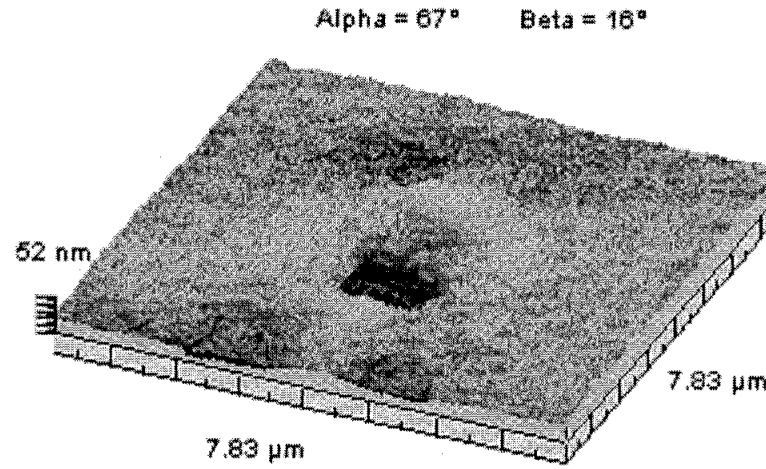
SEM-EDS:
Ca, O, Cl, S, Sr

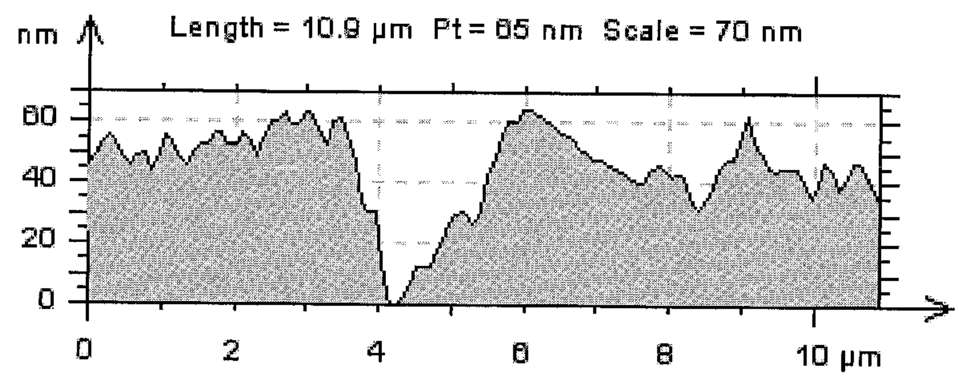




Crater Formation on polished Basalt

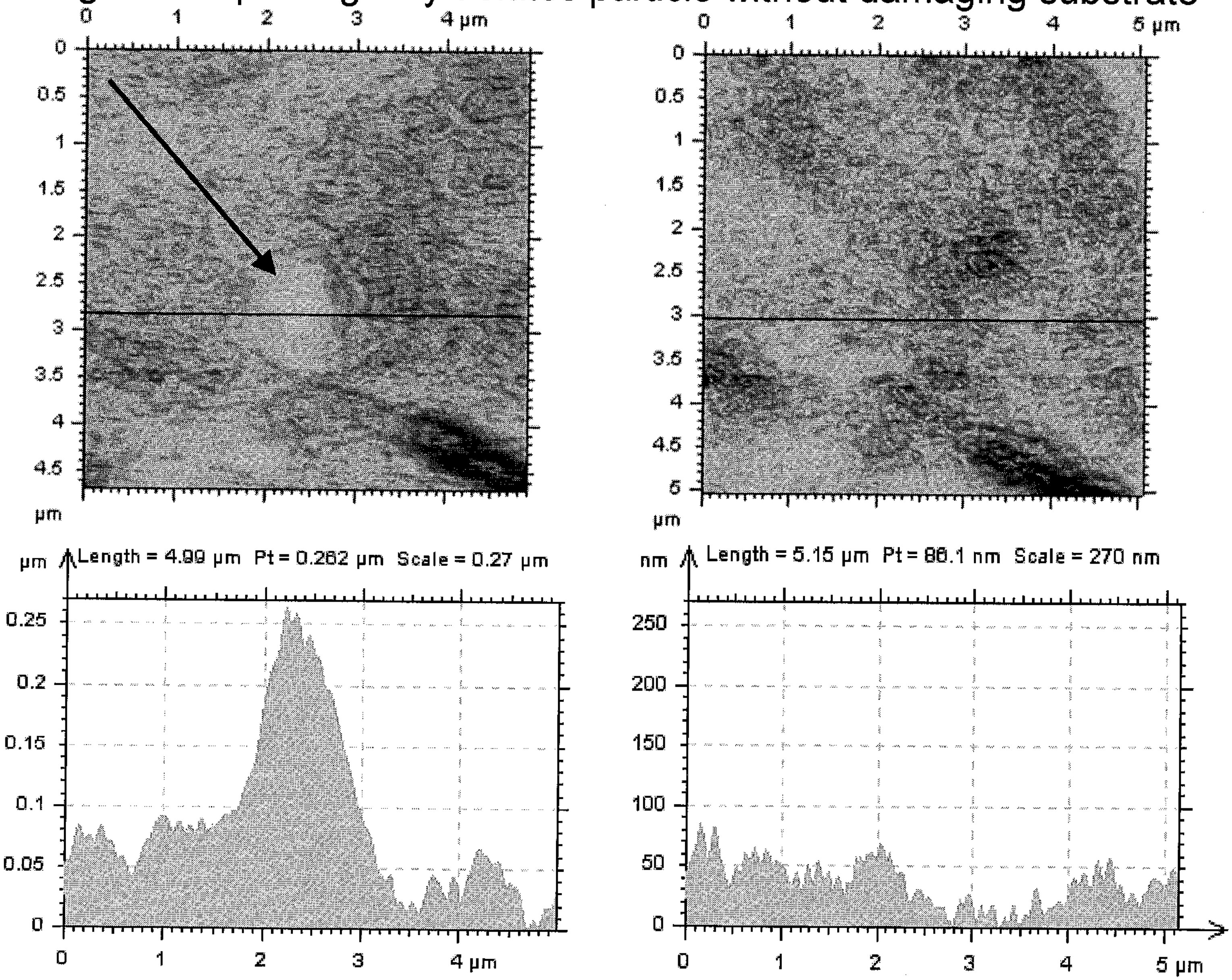






Particle study

Single laser pulse gently ablates particle without damaging substrate



B. subtilis spores on cleaned surface

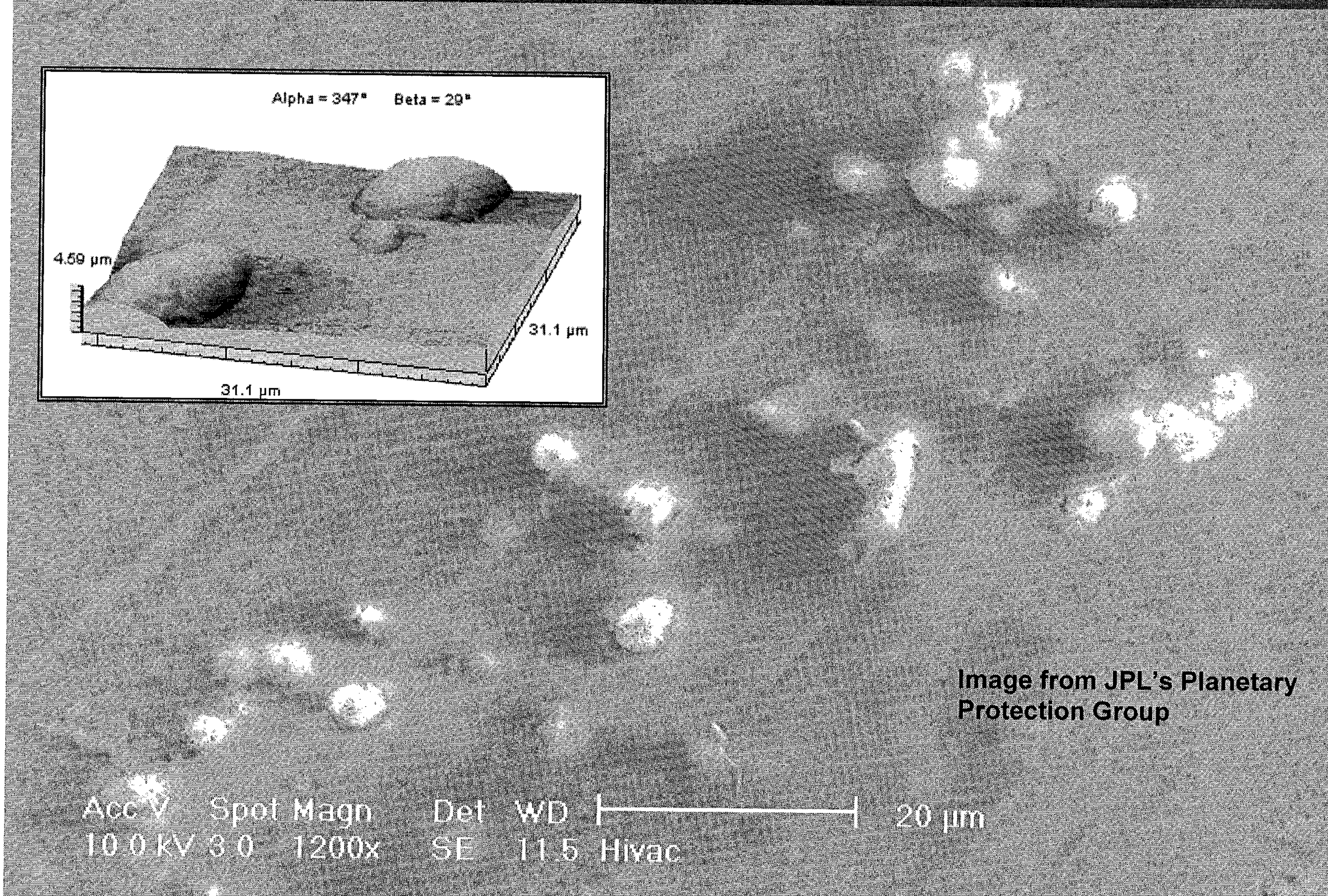
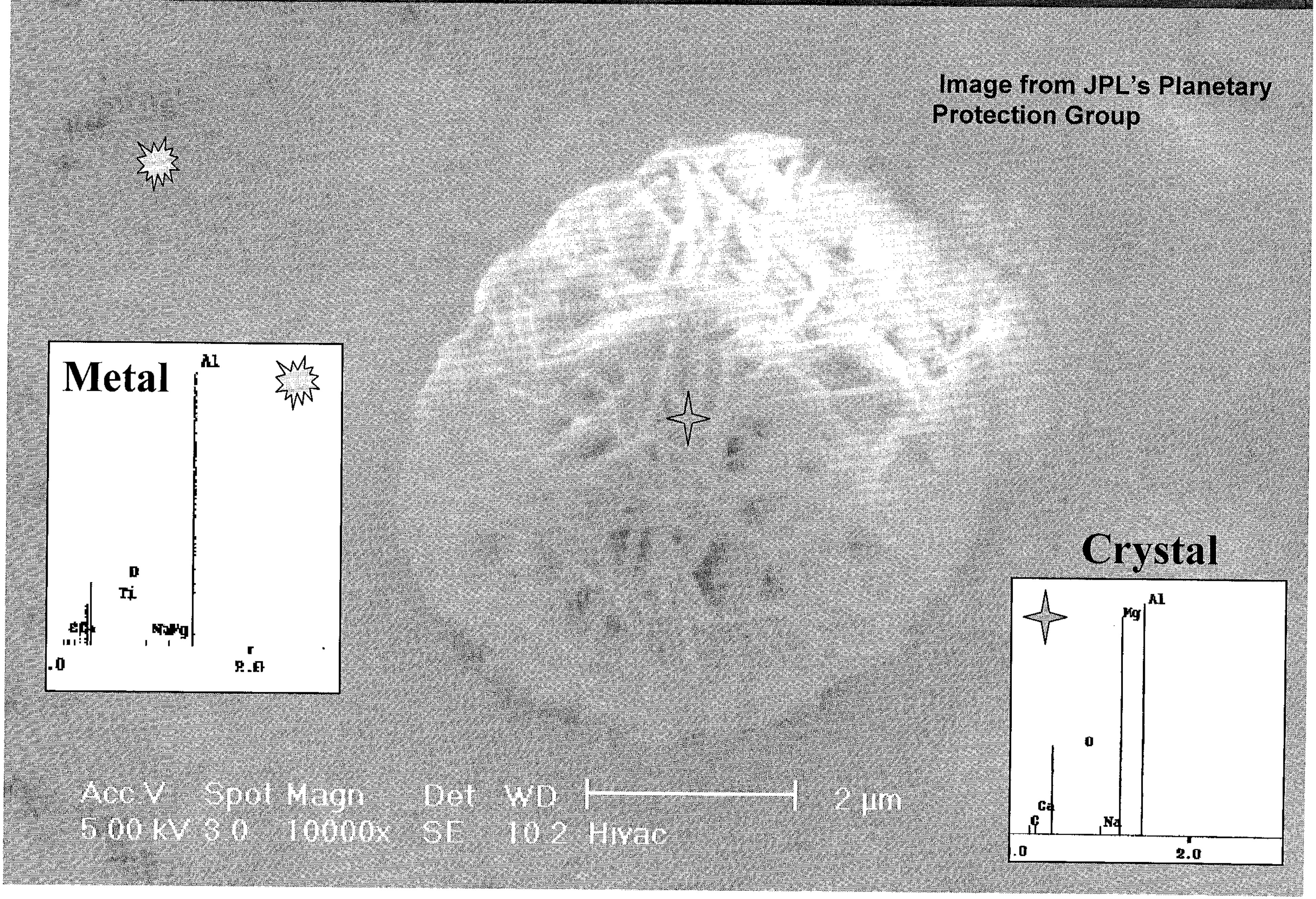


Image from JPL's Planetary Protection Group

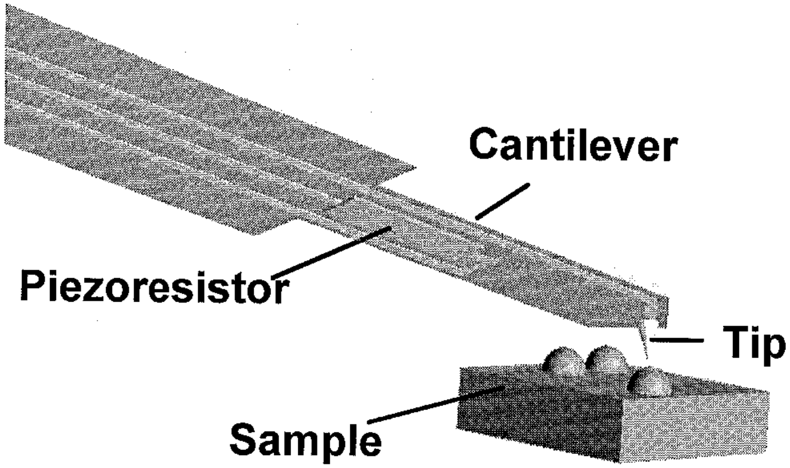
B. subtilis spores on Aluminum

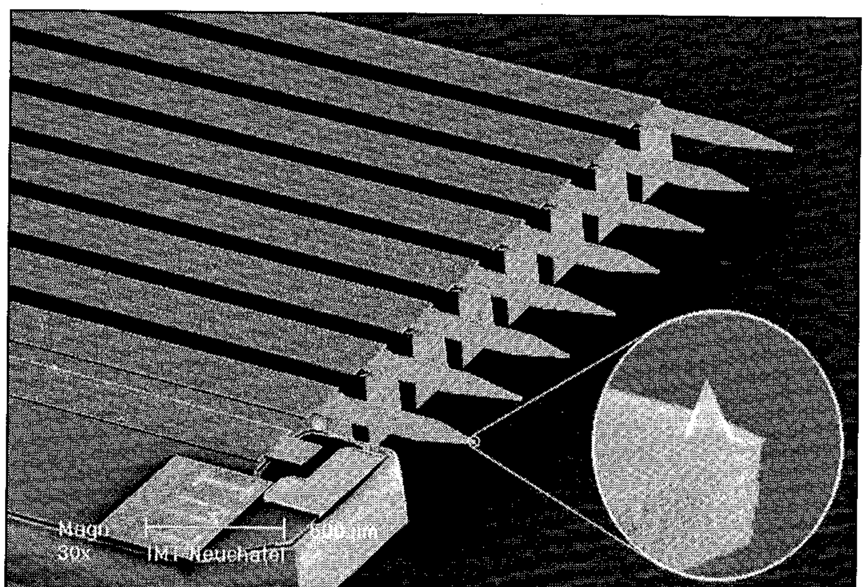


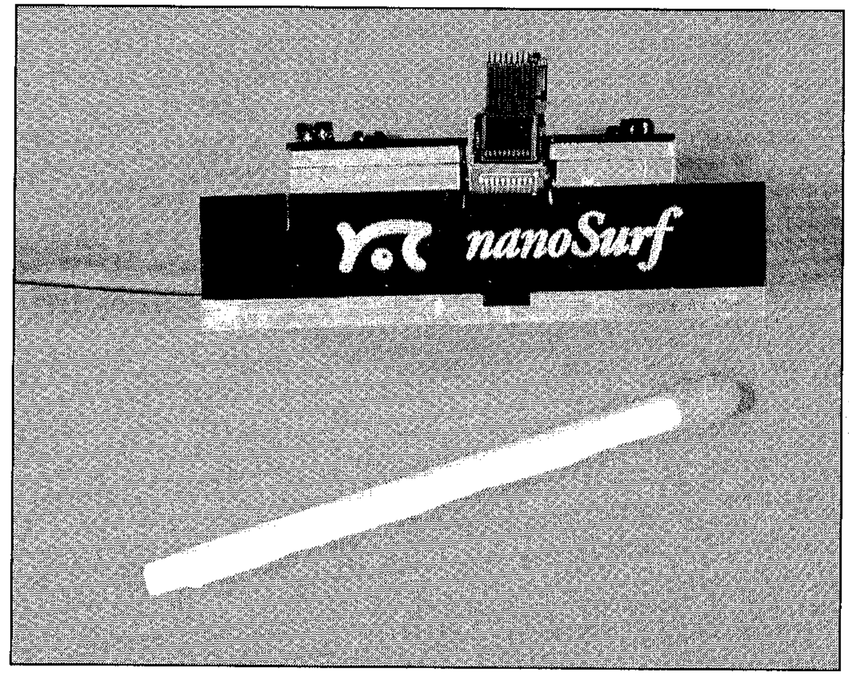
AFM for imaging & spectroscopy

Sensor head

T. Pike & M. Anderson, JPL







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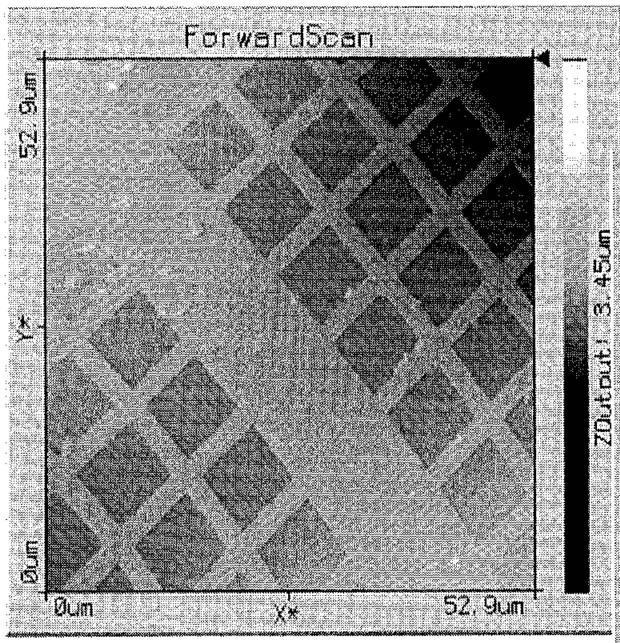
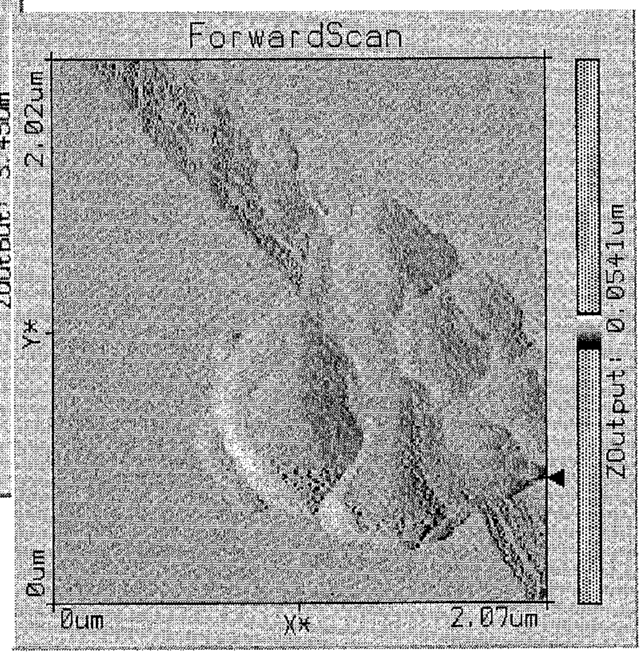
Topographic imaging with AFM

MECA AFM images



Large scan of calibration substrate with dust particles



High-resolution scan of silicon etchant feature in calibration substrate

Scan of fragment of diatom

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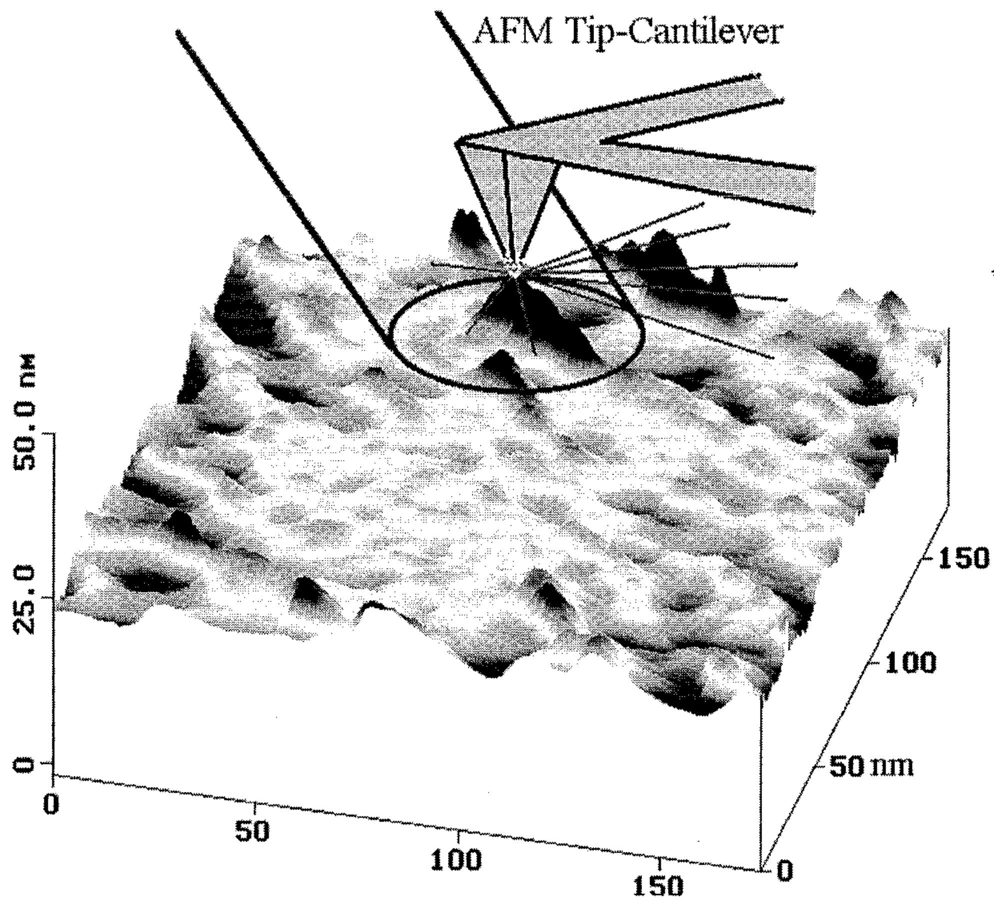
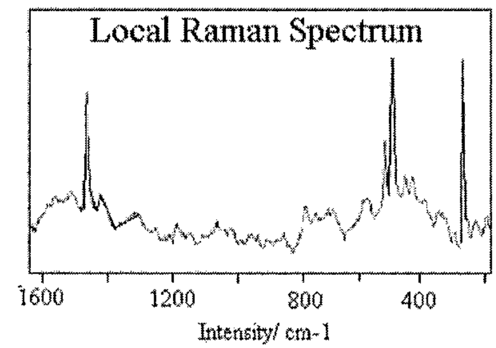
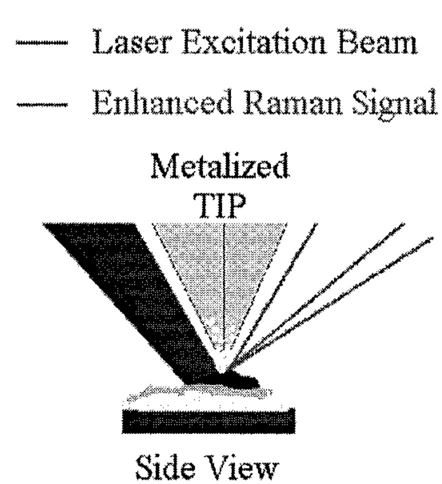
Surface-Enhanced Raman with AFM







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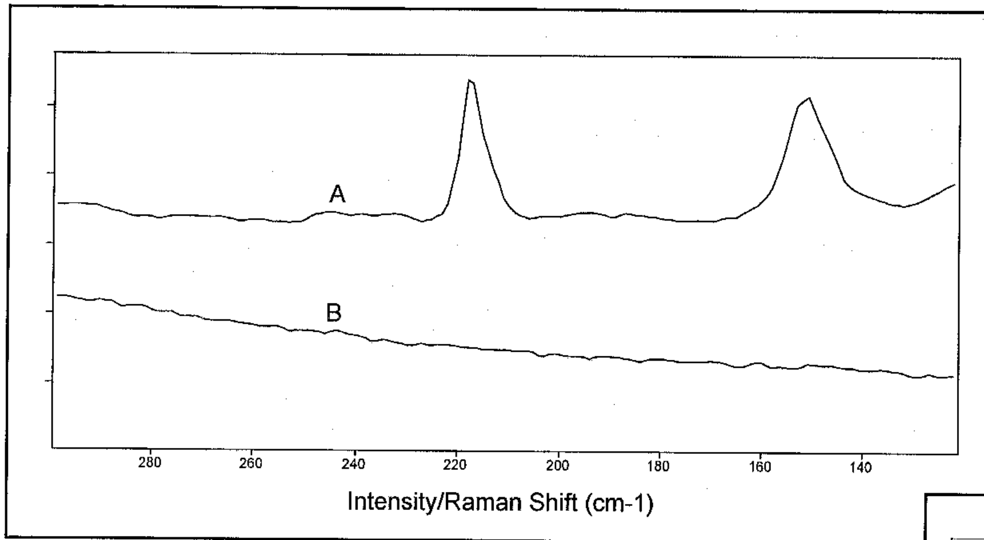
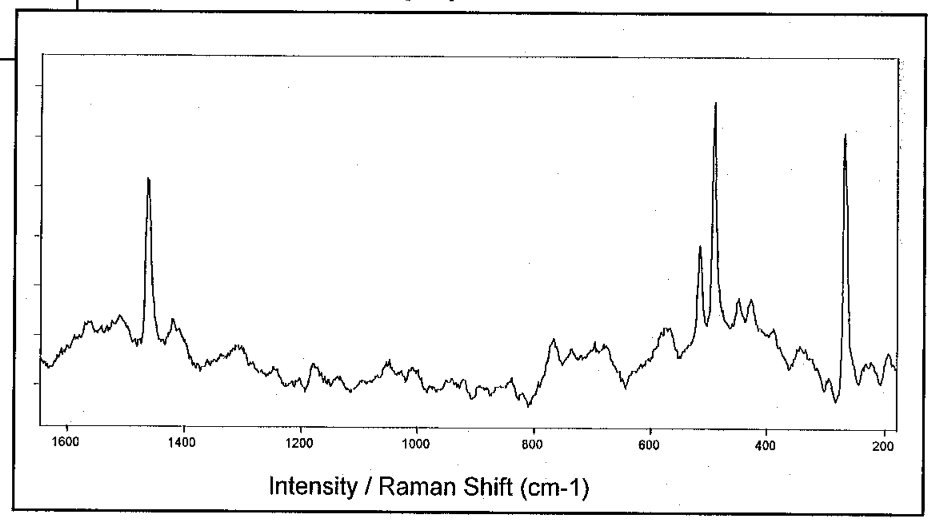
AFM for surface-enhanced Raman



Gold-coated AFM tip generating a local surface enhanced Raman effect on a 10 µm sulfur film (A).

When the beam is focused away from the tip on the film, the Raman signal is undetectable using the same microprobe parameters (B).

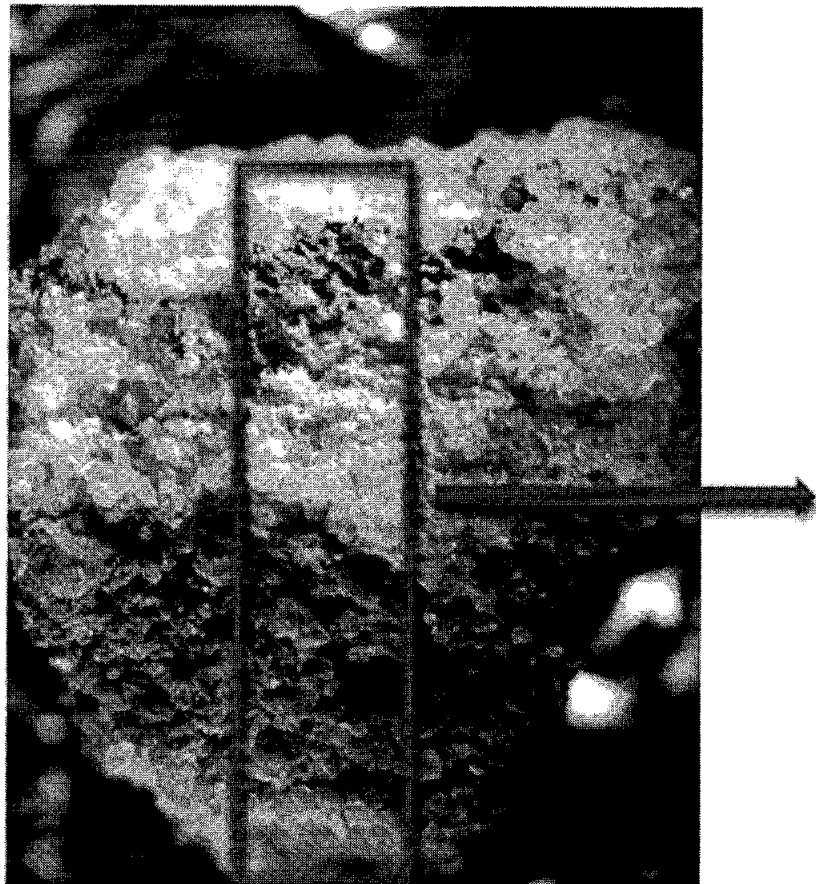
Raman spectrum of ~10 femtograms residue from the surface of a C_{60} sample surgically removed with AFM tip.

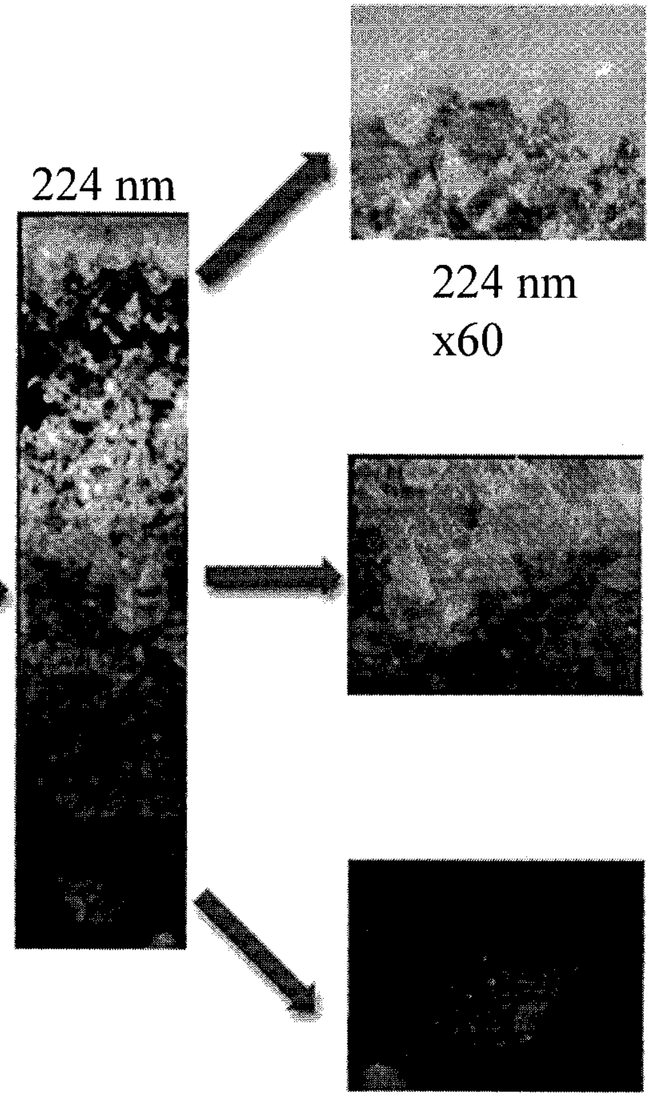


- AFM can provide quantitative topographic imaging down to a few nanometers resolution in a modest resource envelope
- Chemical information is accessible through an IR-AFM combination well below a micron resolution

Laser-induced fluorescence in microbial colonies

224 nm wavelength induces native fluorescence activity in aromatic amino acids.

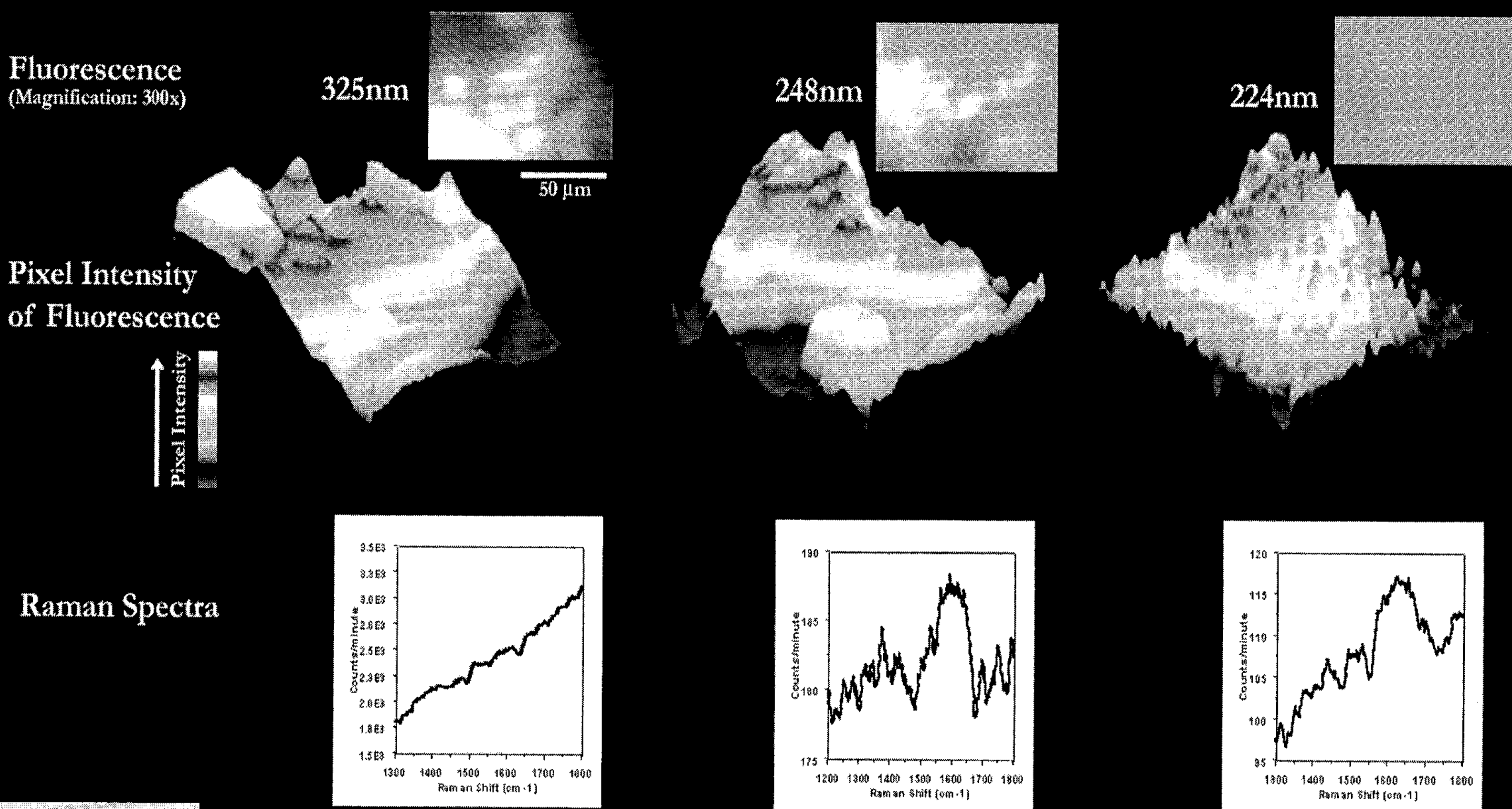




Stratified layering below crust characteristic of cryptoendolithic communities

P. Conrad/JPL

Deep Ultraviolet Laser Induced Fluorescence and Raman Spectroscopy of the Algal Community within an Antarctic Rock



P. Conrad/JPL

Portable UV fluorescence imaging & Raman

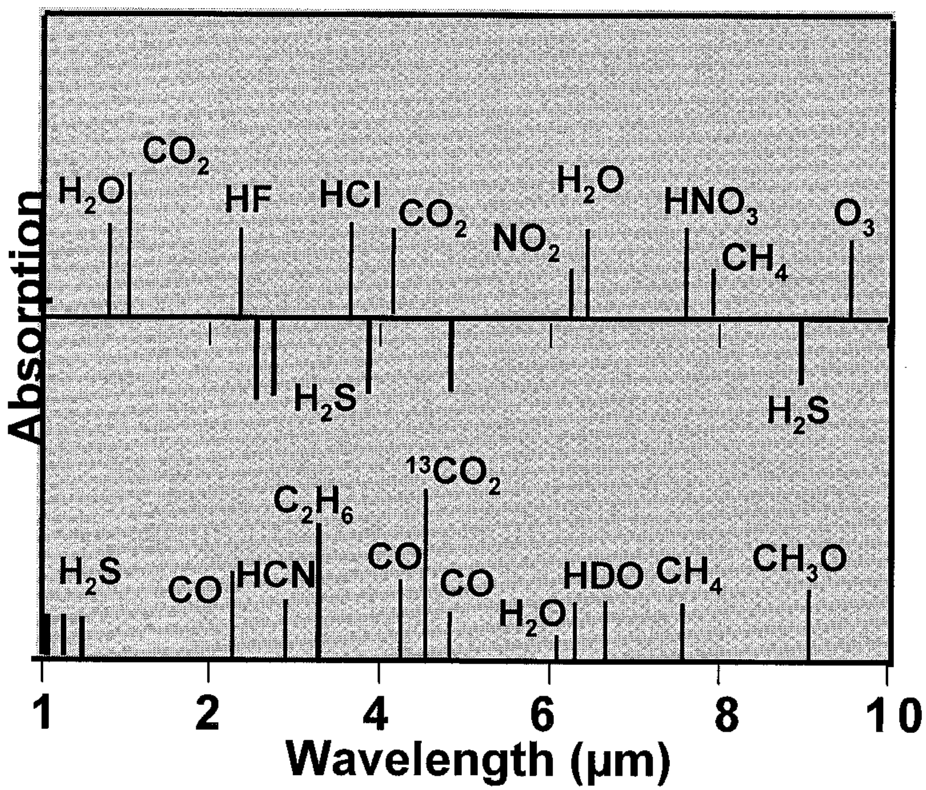
20 cm X 25 cm X 50.8 cm — 10 kg

224 nm, 248 nm, 325 nm — < 100 W

P. Conrad/JPL
W. Hugs/Photon Systems

Infrared lasers for chemical analysis

Laser-based instruments that cover 2–12 μm will enable the detection of all gases & volatiles of interest for planetary exploration, including isotopes—



- Gas evolution from rock, soil, or ice samples (e.g. CH_4, NH_3, HCN, HCL_3, CO_2)
- Atmospheric composition
- Isotopic ratios $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{17}O/^{16}O$, $^{15}N/^{14}N$, H_2O/HDO
- ppb sensitivities

Laser spectroscopy first on MPL

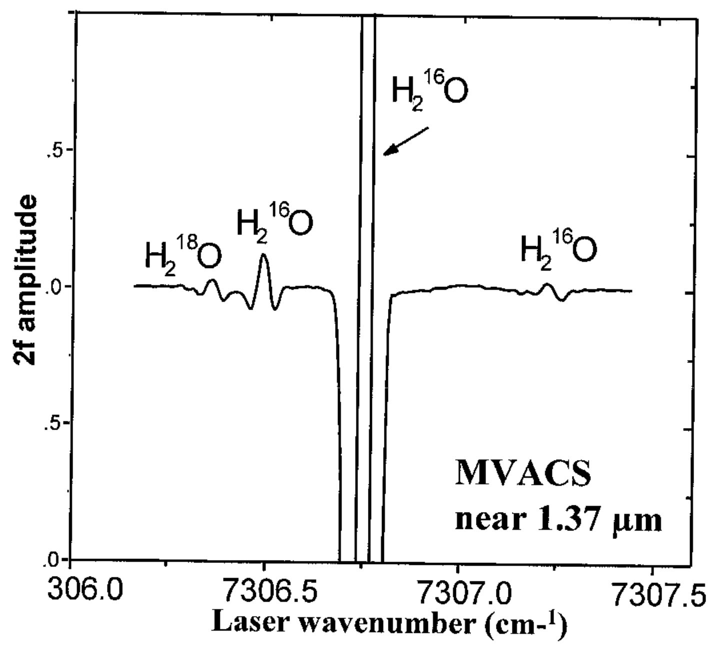
MVACS carried 4 TDLs

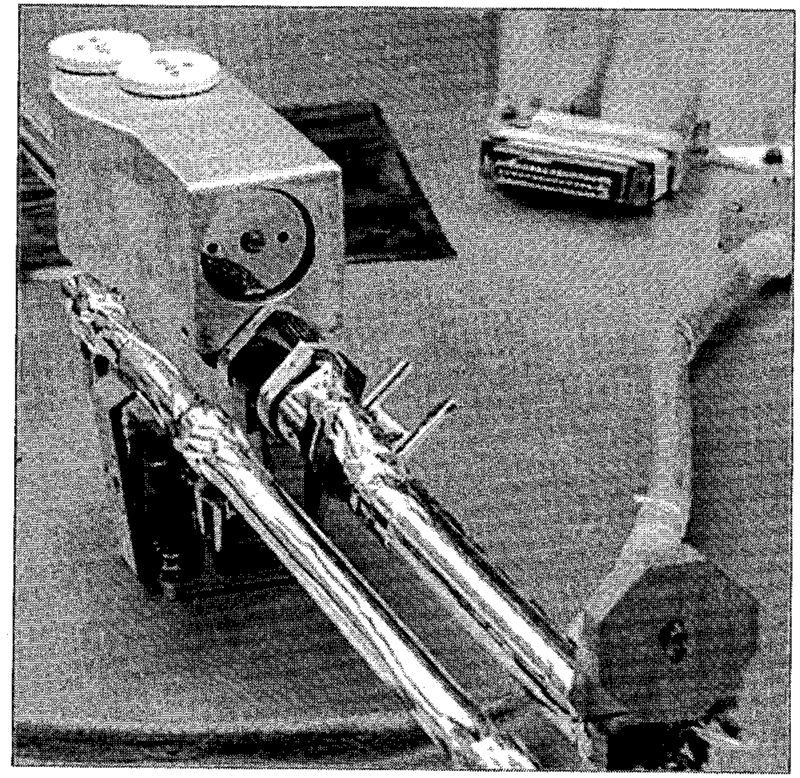
- Meteorology package to measure water content of Mars atmosphere

  1.37 µm (H_2O, 1 ppm)

- Thermally Evolved Gas Analyzer (TEGA) to measure volatile components of soil

  1.37 µm & 2.04 µm (CO_2 isotopes)



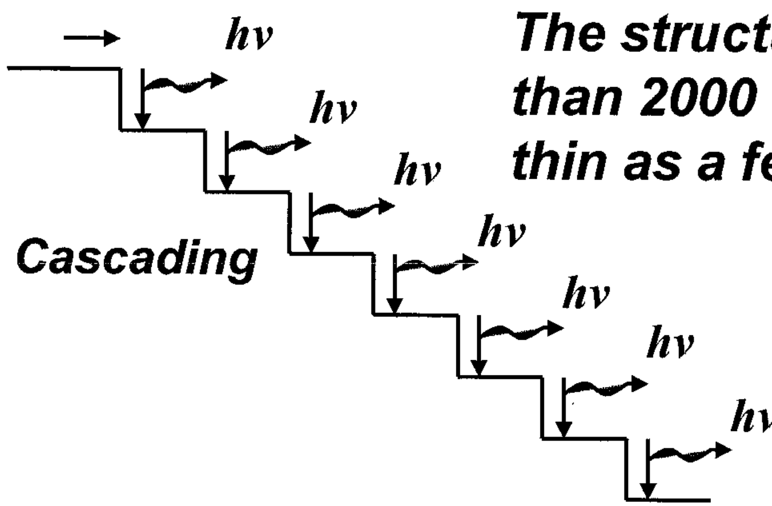


Miniature laser spectrometer for the measurement of CO_2 & H_2O isotopes in the Martian atmosphere.

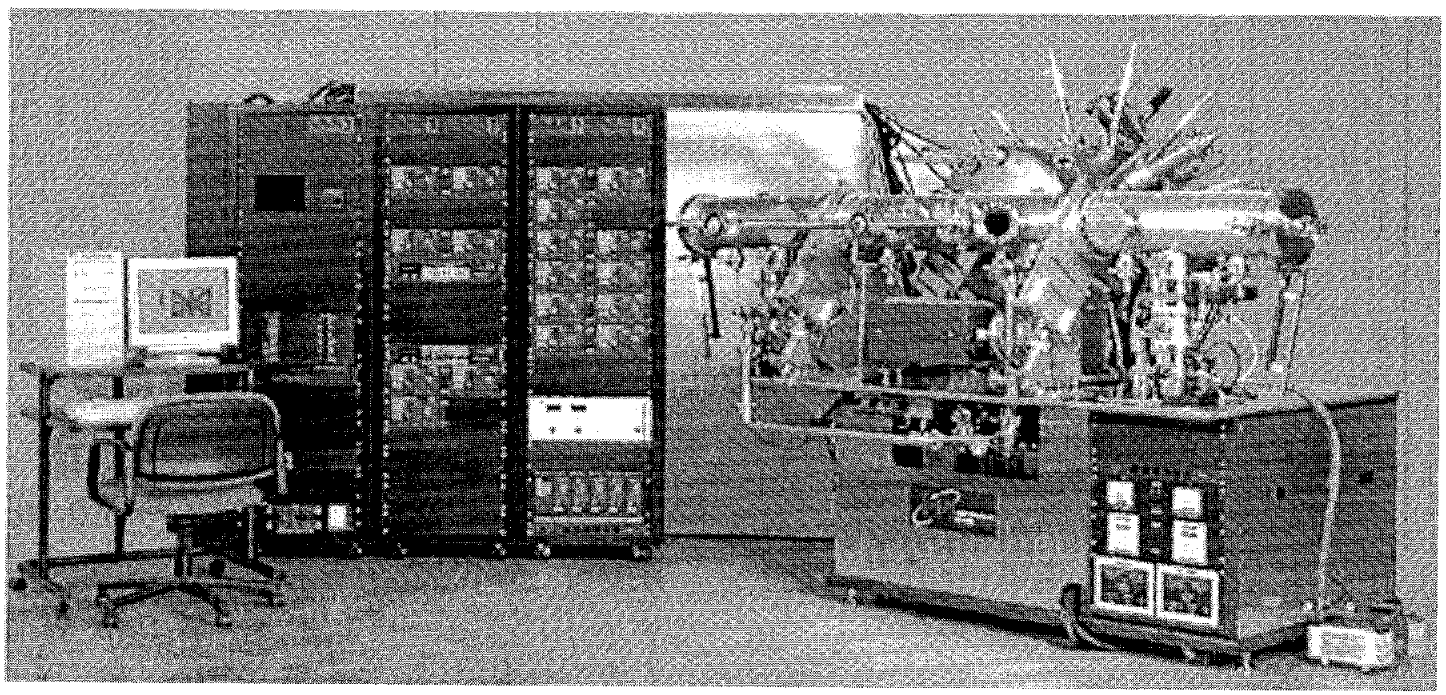
DS2 penetrator probe

- to measure subsurface water in Mars soil

2–10 μm Interband cascade lasers



The structure is complicated—more than 2000 epitaxial layers, some as thin as a few atomic layers!



Sample Preparation

Examples:

EXPERIMENT	ANALYTICAL TOOL	SAMPLE HANDING/PREP
Viking biology	Scintillation, GCMS	Soil sieved, solution added, heated
MVACS (TEGA)	Molecular absorption spectroscopy	Soil sieved, heated
DS-2	Molecular absorption spectroscopy	Soil heated
MSL	Raman, Mossbauer (examples)	Rock grinder/sorter
'01 MECA	Electrochemistry (canceled)	Solution & calibrants added, stirring

- Our in situ instruments flown to date (or about to fly) have involved sensor systems that require no or simple, minimal sample handling & preparation
- Scooping or drilling used to deliver sample to instrument.

Future Sample Handling

EXAMPLE ANALYTICAL TOOLS

Emerging "on-chip" detectors

- *Biosensors*
- *Electrochemical*
- *Integrated electro optical*
- *Polymeric artificial antibodies*

Emerging micro analytical tools

Need increasingly sophisticated miniaturized lab-bench procedures for "dry" and "wet" micro analytical systems

SAMPLE HANDING & PREPARATION

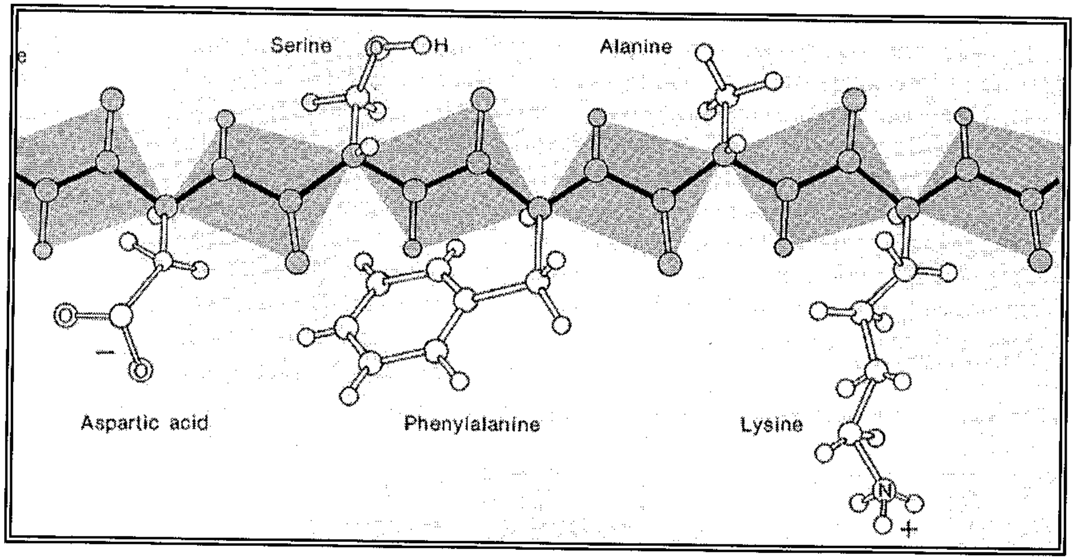
Wet chemistry procedures

- *Separations*
- *Reactions, derivatizations*
- *Reagent preparation*
- *Volumetric metering*
- *Mixing*
- *Fluid positioning*
- *Filtering, concentrating,*
  Heating, cooling
- *Washing, storage...*

Dry preparation procedures

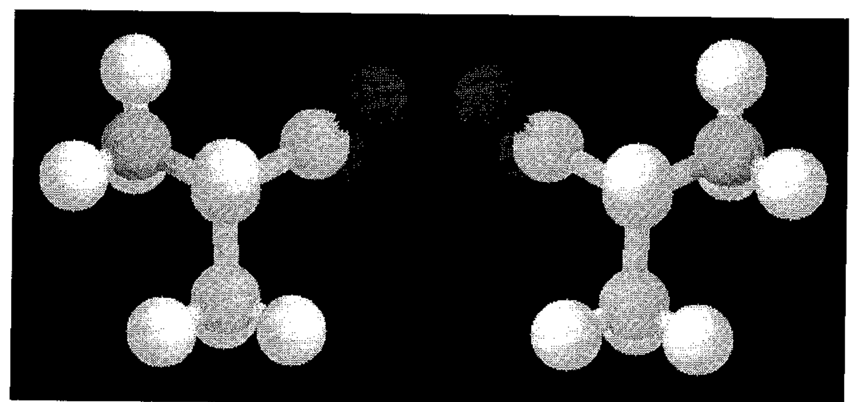
- *Cutting, polishing, sectioning*
- *Separation by physical & chemical properties*
- *Sublimation*

Looking for Amino Acids



- They are readily synthesized under plausible prebiotic conditions
- Long lifetime under dry, cold conditions
- They are abundant in carbonaceous chondrites
- Molecular architecture can be used to distinguish abiotic versus biotic origins

- **Abiotic chemistry**
  - Presence of non-protein amino acids and racemic amino acids
- **Extinct life**
  - Amino acids with different amounts of racemization
- **Extant life**
  - Amino acid homochirality



L-alanine **D-alanine**

Composition and Chirality Analysis through CE

- In CZE, EOF sweeps all molecules to the cathode

- CE separates amino acids based on charge/size ratio

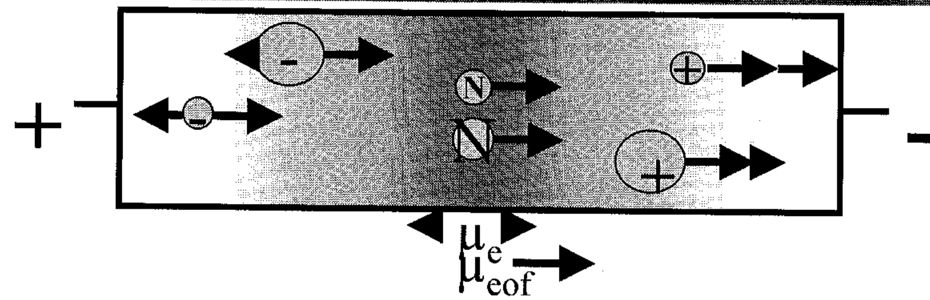
- L and D-amino acids are not resolved because of identical mobilities

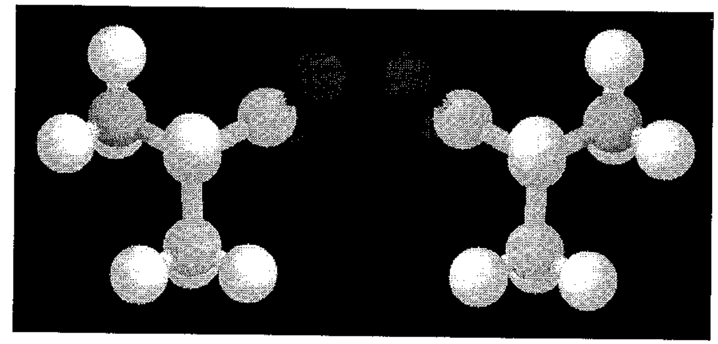
- Cyclodextrins provide enantiomeric resolution of amino acids because of different complexation constants and altered size when complexed:

$$\text{L-aa} + \text{CD} \leftrightarrows \text{L-complex} \ (K_L)$$
$$\text{D-aa} + \text{CD} \leftrightarrows \text{D-complex} \ (K_D)$$

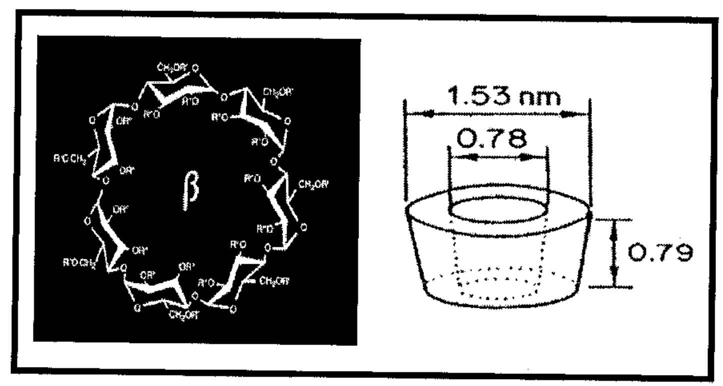
$$K_L \neq K_D$$

- The net apparent mobilities μ_a are different
  - $\mu_L \neq \mu_D$





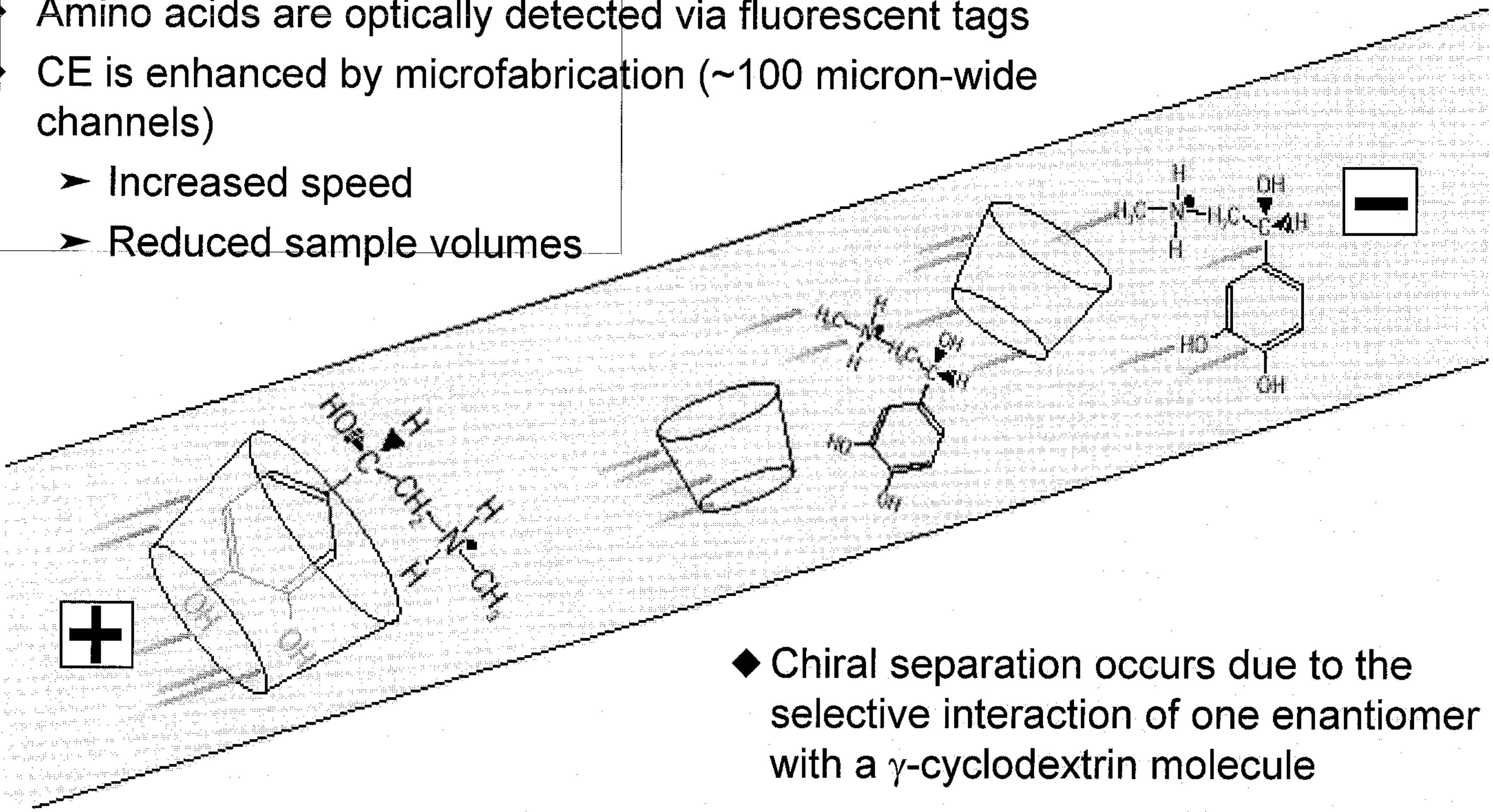
L-alanine D-alanine



cyclodextrin

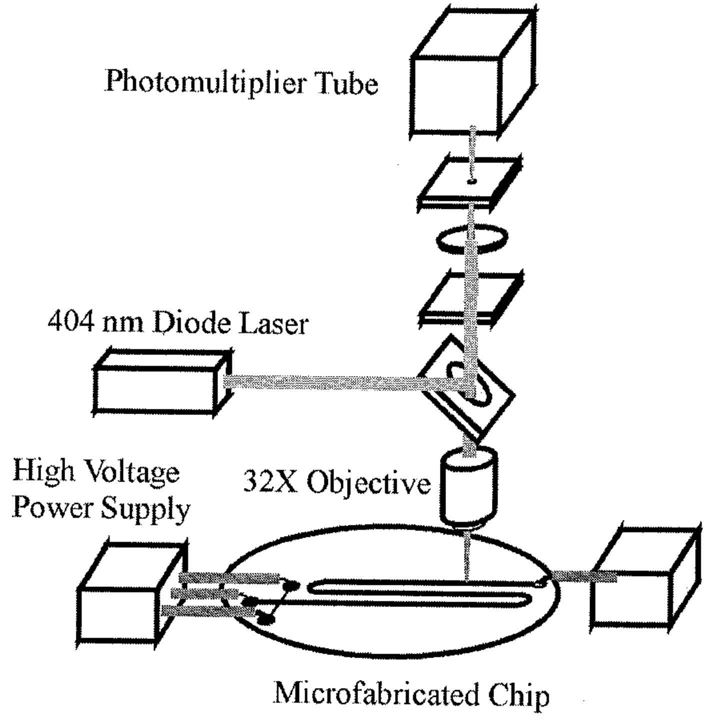
μCapilliary electrophoresis

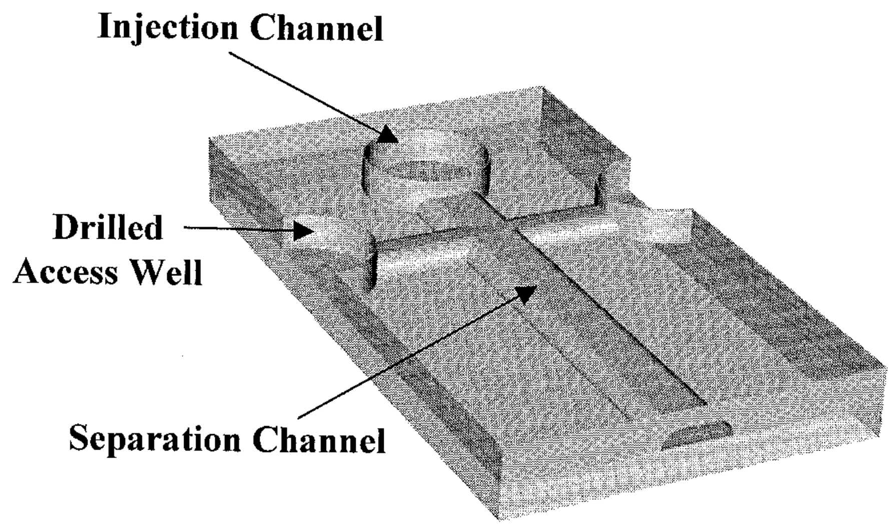
- Amino acid composition and especially chirality is a possible probe for extinct or extant life in extraterrestrial environments.
- Microfabricated devices are now available that can determine amino acid composition and chirality in minutes on only nanoliters of sample.
- Amino acids are optically detected via fluorescent tags
- CE is enhanced by microfabrication (~100 micron-wide channels)
  - ➢ Increased speed
  - ➢ Reduced sample volumes



- Chiral separation occurs due to the selective interaction of one enantiomer with a γ-cyclodextrin molecule

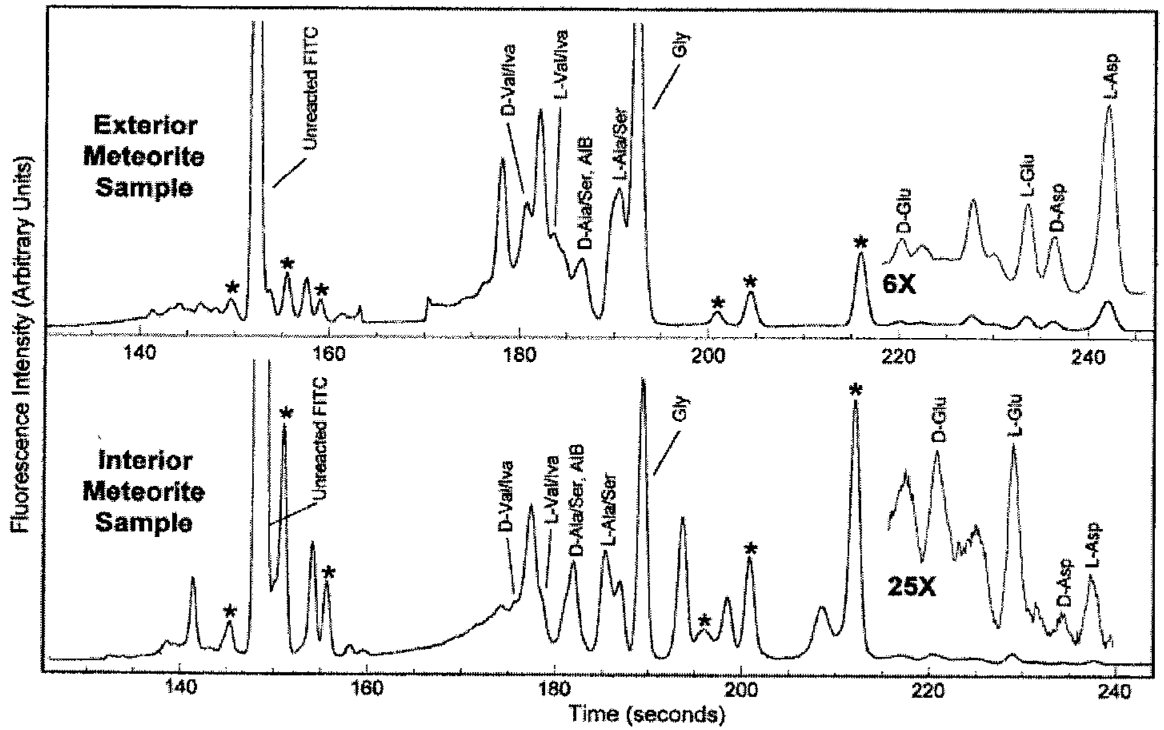
Separation and Detection System





- The test system consists of a folded electrophoresis channel (19.0 cm long x 150 mm wide x 20 mm deep) photolithographically fabricated in a 10 cm-diameter glass wafer sandwich.
- A laser-excited confocal fluorescence detection apparatus provides sub-attomole ($<10^{-18}$ mole) sensitivity {Hutt et al. *Anal. Chem* **71, 4000 (1999)**}.

μCE analysis of Murchison Meterite



Murchison Asp and Glu D/L Ratios

Asp = aspartic acid

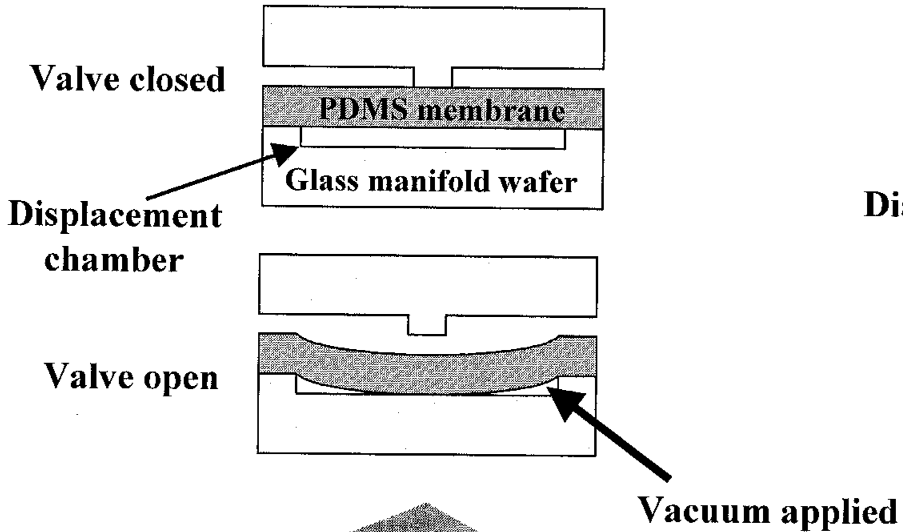
Glu = glutamic acid

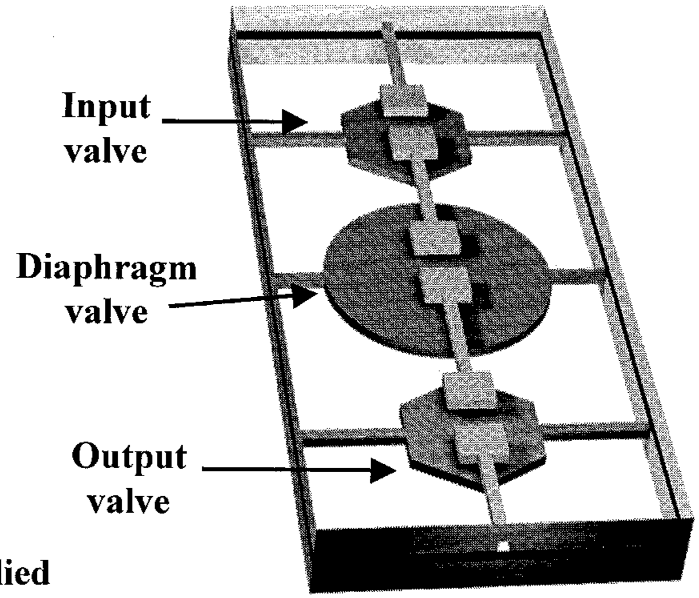
Amino acid	microchip	HPLC
Glu exterior	**0.33 ± 0.04**	**0.3 ± 0.1**
Glu interior	**0.65 ± 0.07**	**0.7 ± 0.1**
Asp exterior	**0.21 ± 0.03**	**0.3 ± 0.1**
Asp interior	**0.30 ± 0.06**	**0.3 ± 0.1**

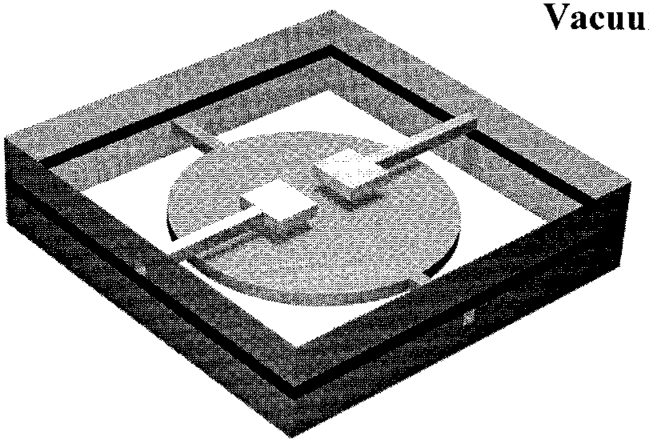
Hutt, Glavin, Bada and Mathies, *Anal. Chem.* 71, 4000–4006 (1999)

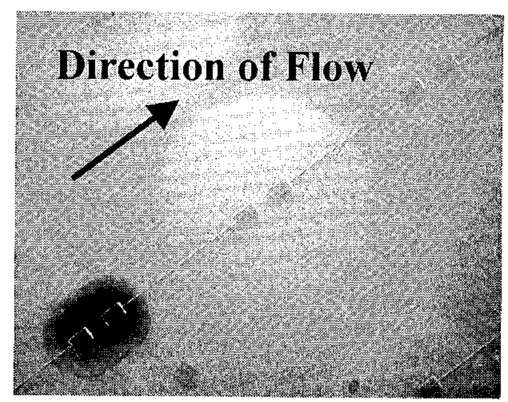
Microfabricated Valves and Pumps

Side View





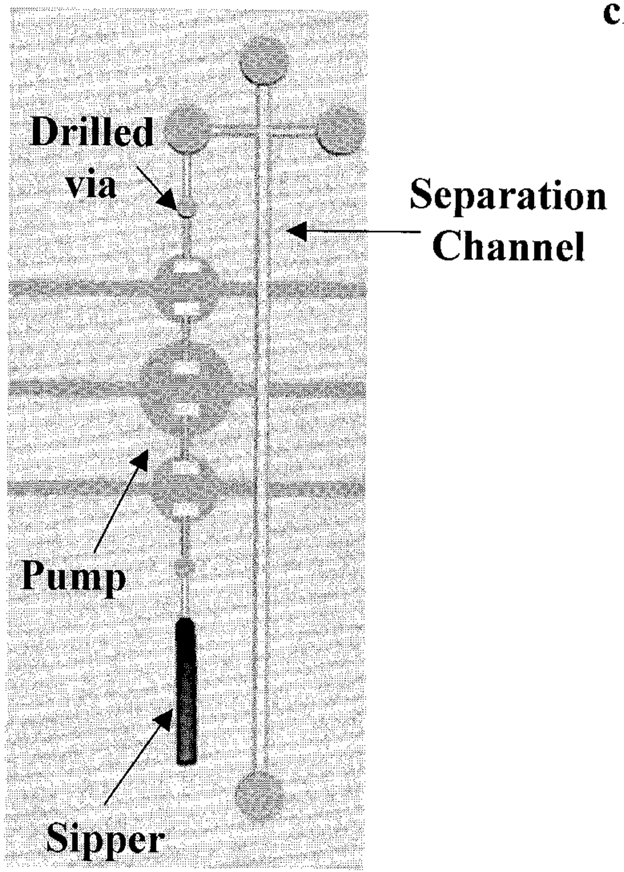




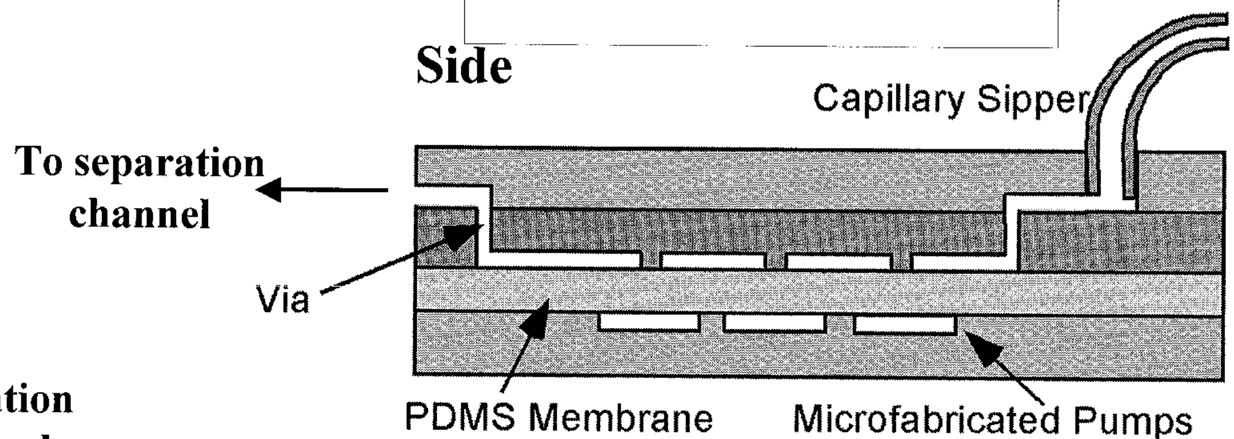
- Pump 10 nL to 10 uL per actuation
- Flow rates from 1 to 150 nL/s
- Self-priming, pump against head pressures

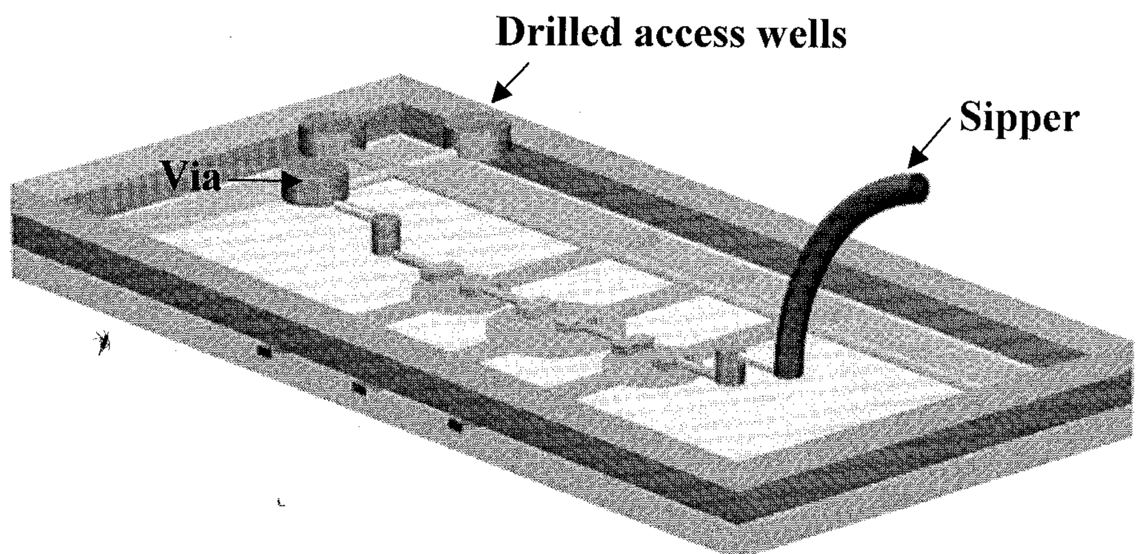
Sample collection to separation

Top

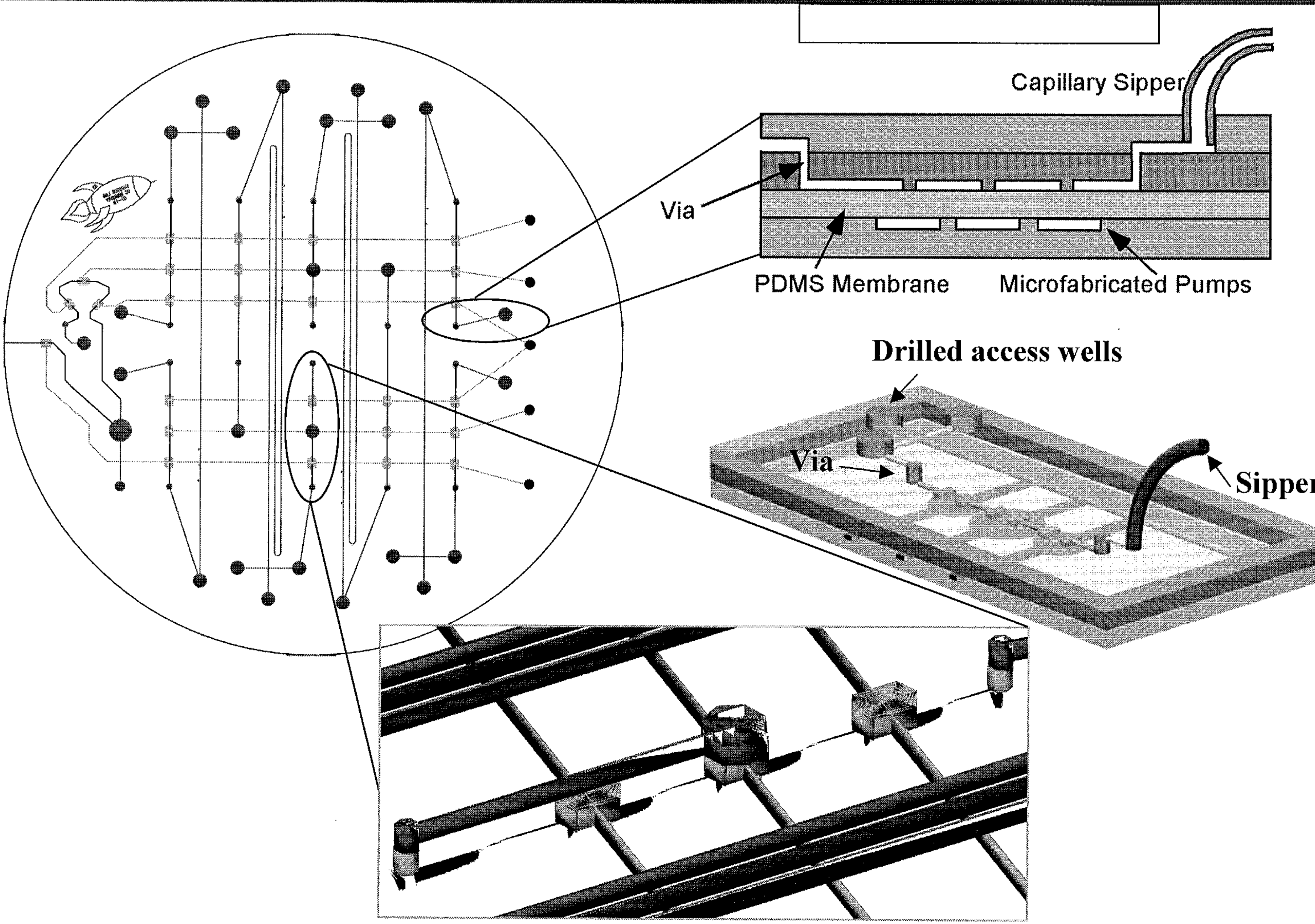


Side



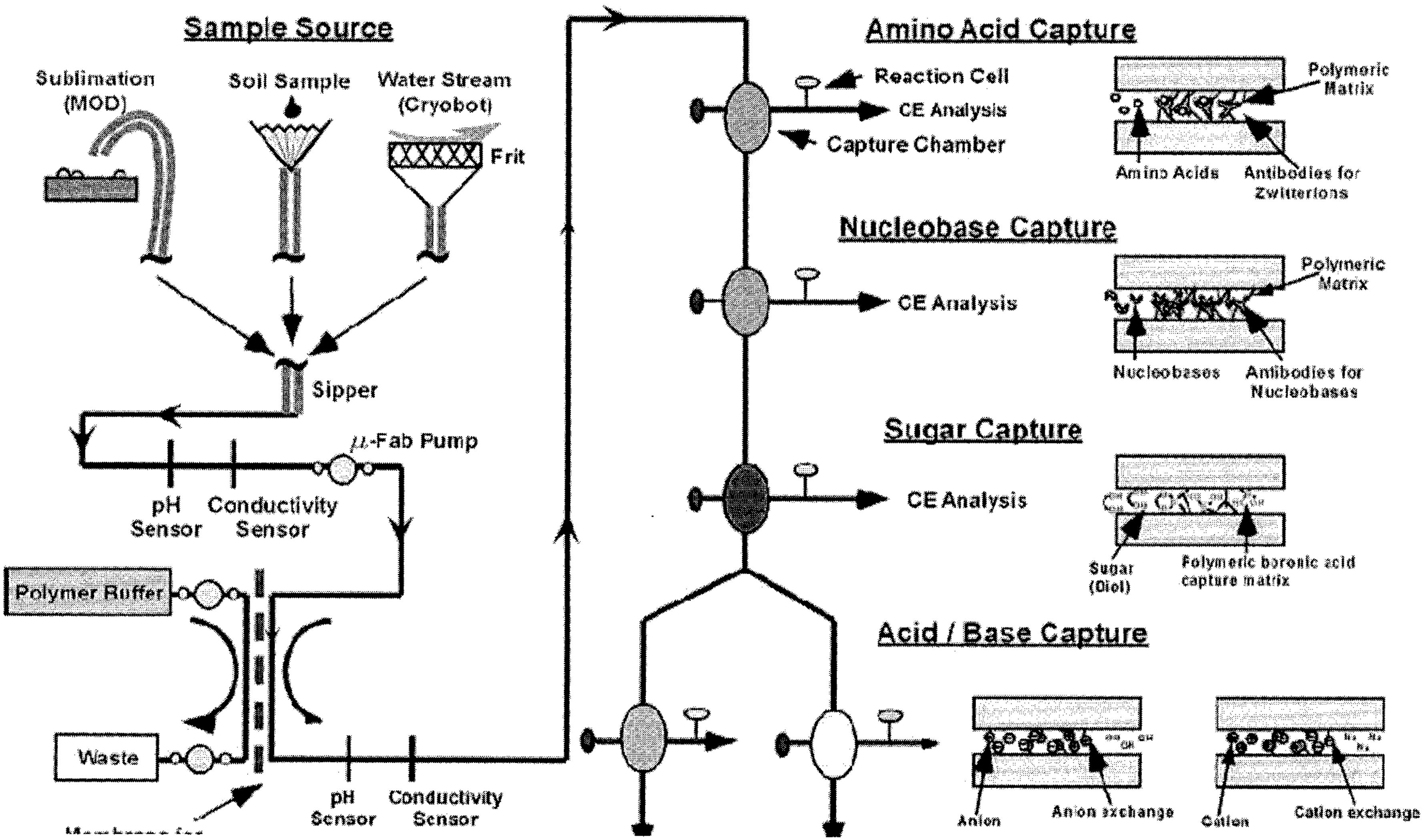


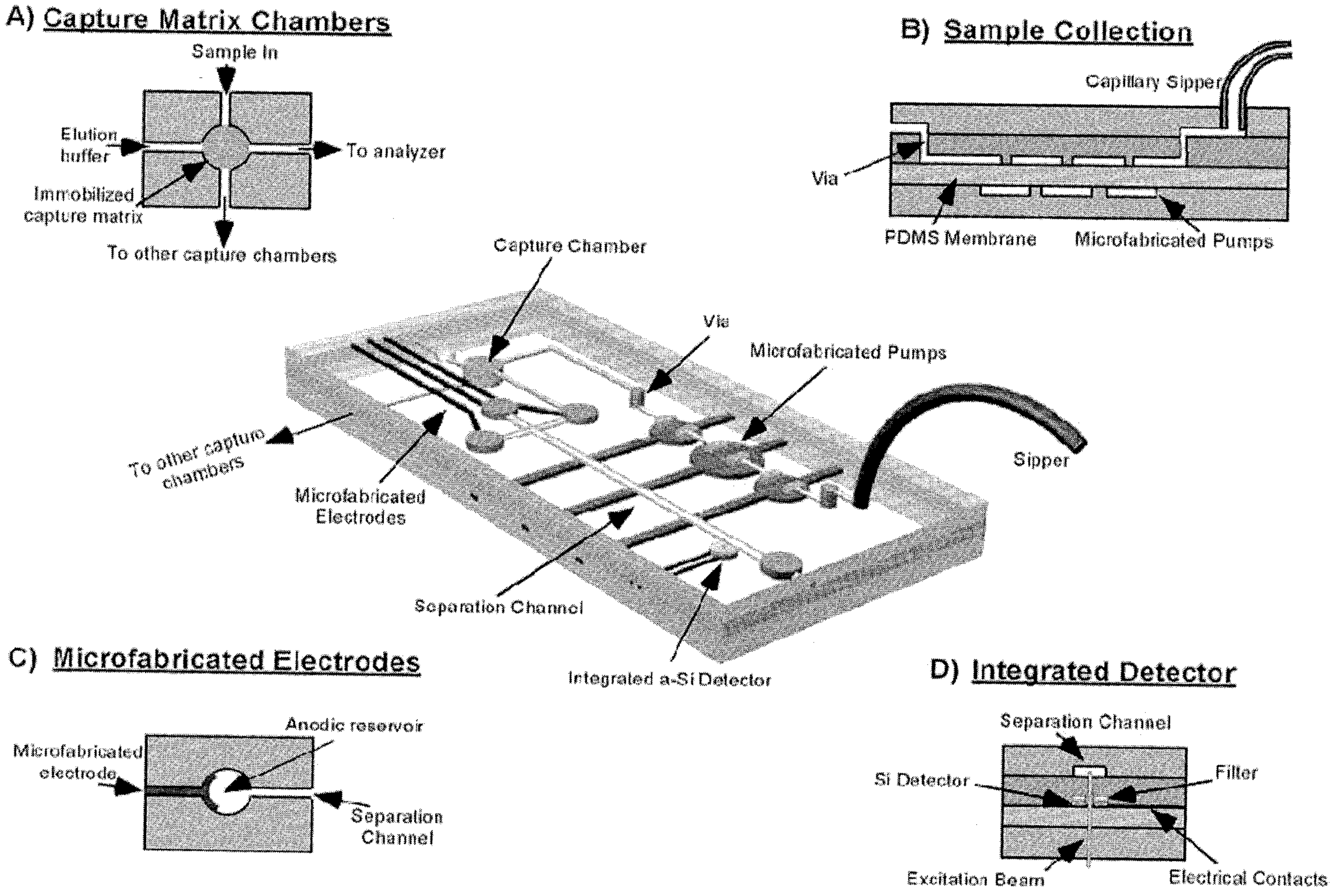
Sample collection to separation



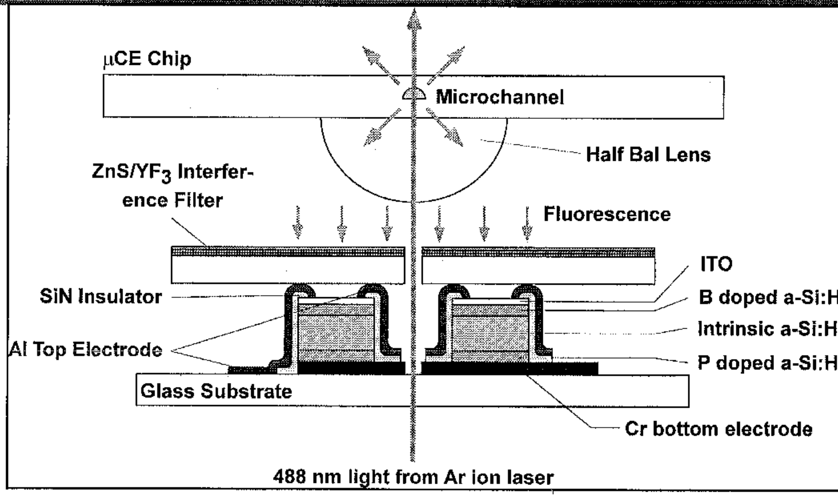
Lab-on-a-chip future concept

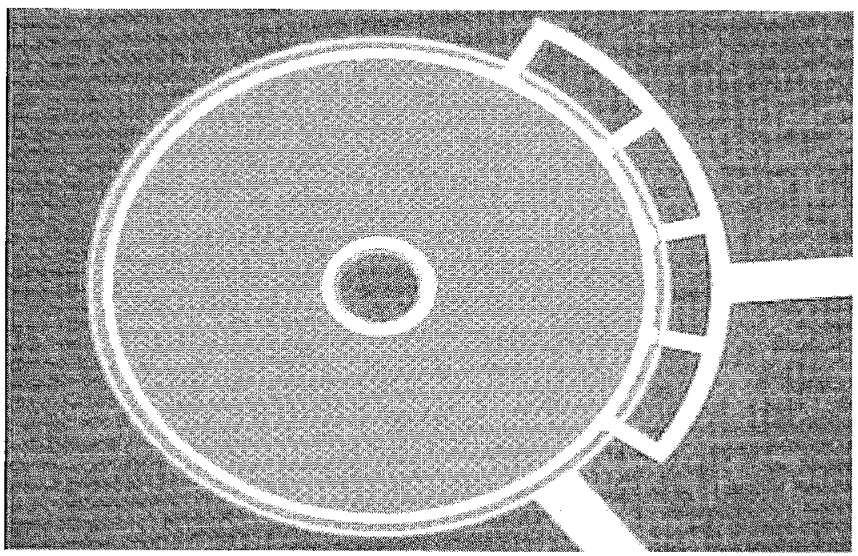
UCB/UCSD/JPL

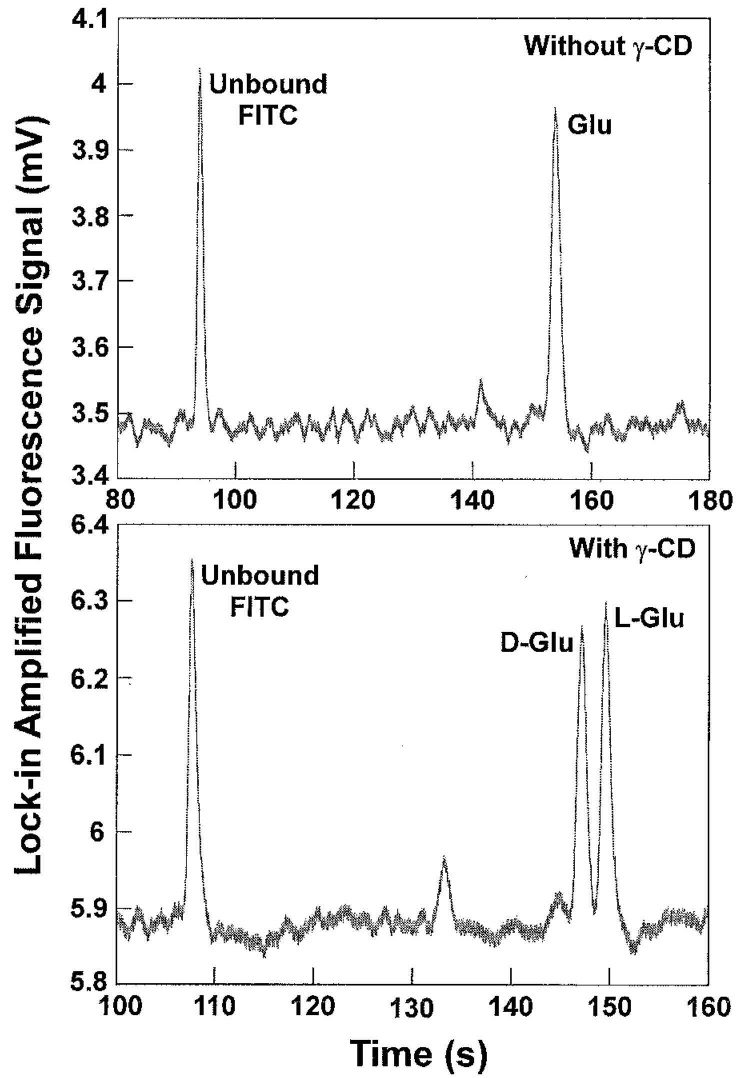



A) Capture Matrix Chambers
Sample In
Elution buffer
To analyzer
Immobilized capture matrix
To other capture chambers
B) Sample Collection
Capillary Sipper
Via
PDMS Membrane
Microfabricated Pumps
Capture Chamber
Via
Microfabricated Pumps
To other capture chambers
Sipper
Microfabricated Electrodes
Separation Channel
Integrated a-Si Detector
C) Microfabricated Electrodes
Anodic reservoir
Microfabricated electrode
Separation Channel
D) Integrated Detector
Separation Channel
Si Detector
Filter
Excitation Beam
Electrical Contacts

Amino Acid Analysis with Integrated Detector

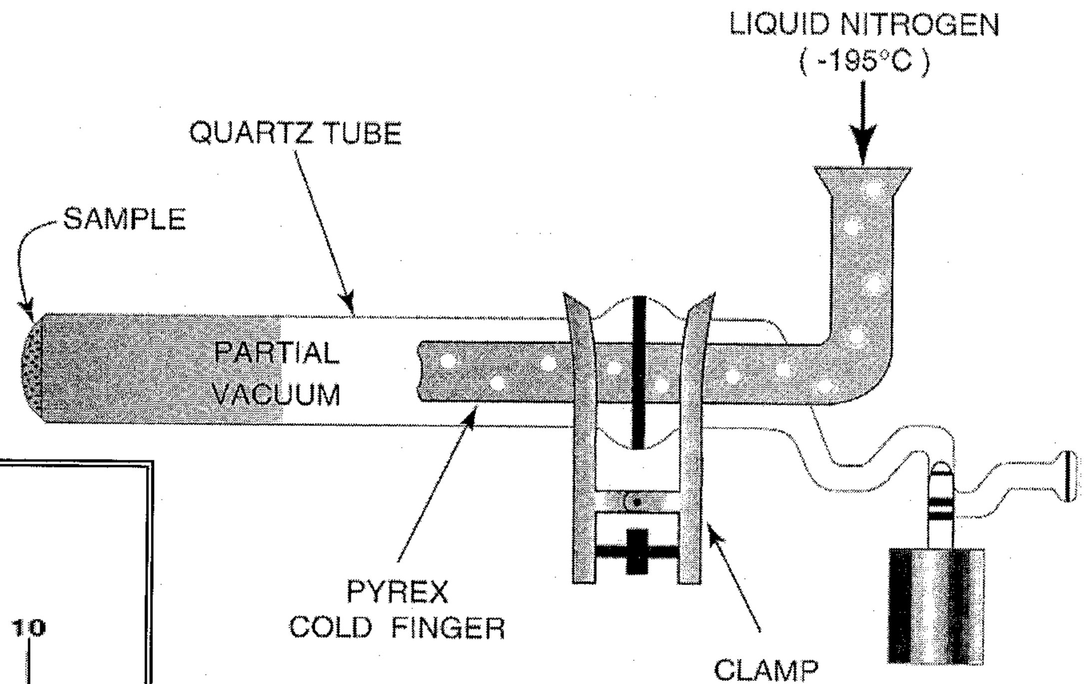


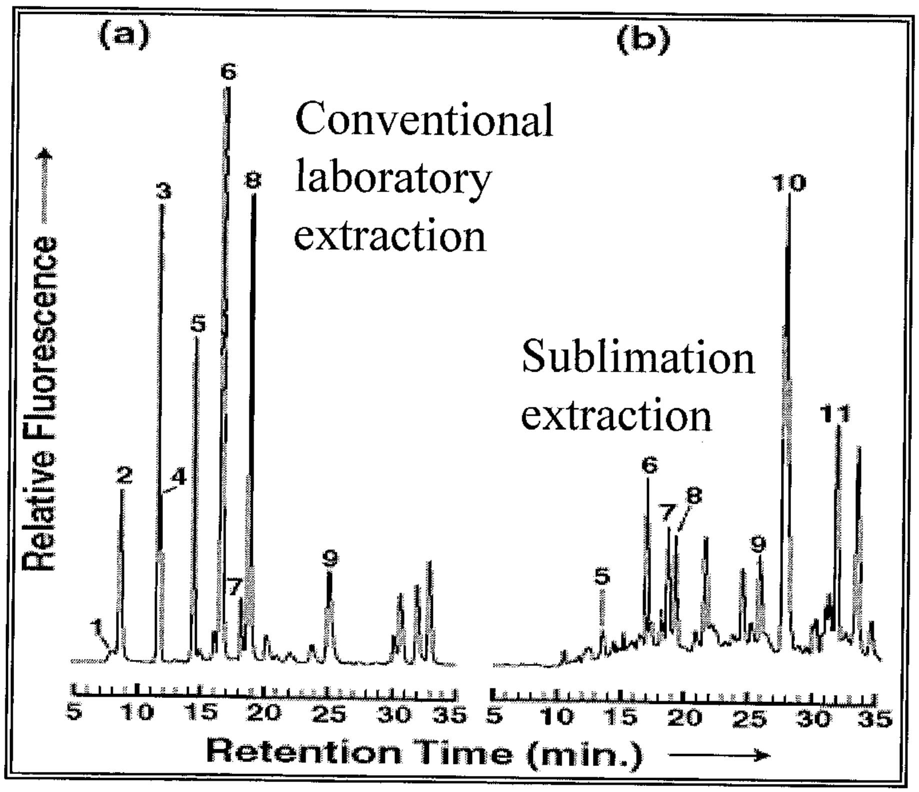




Work performed by Dr. Toshihiro Kamei

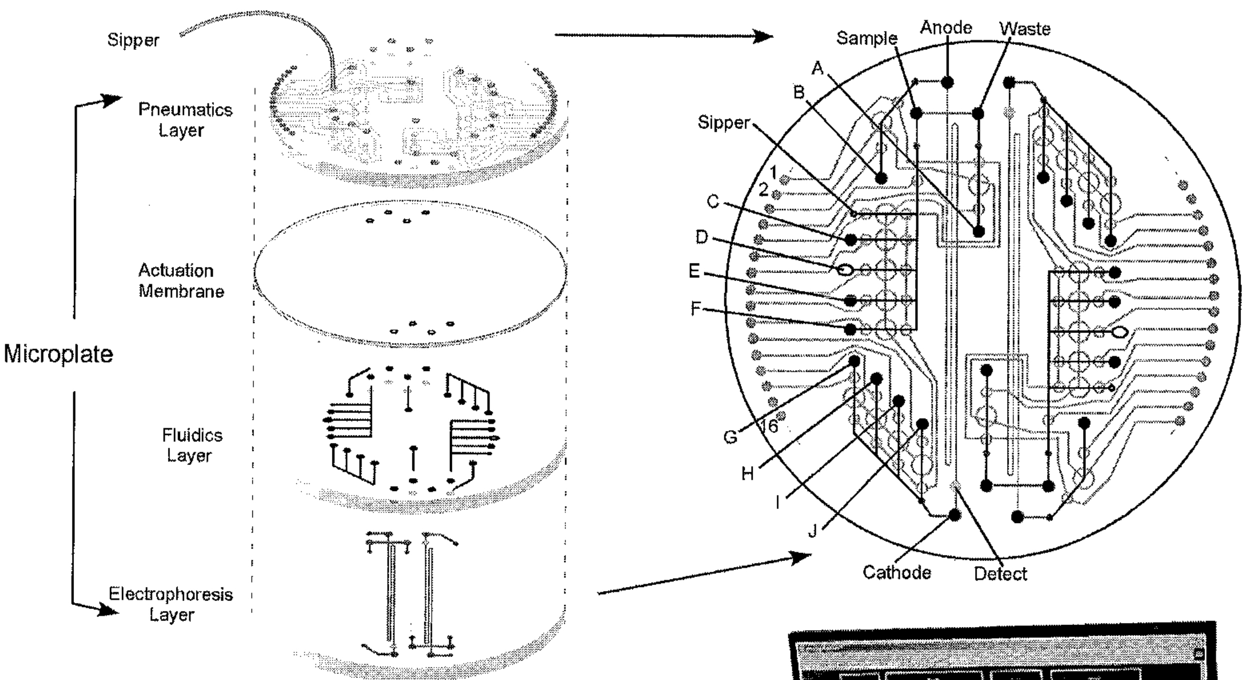
MOD organic extraction

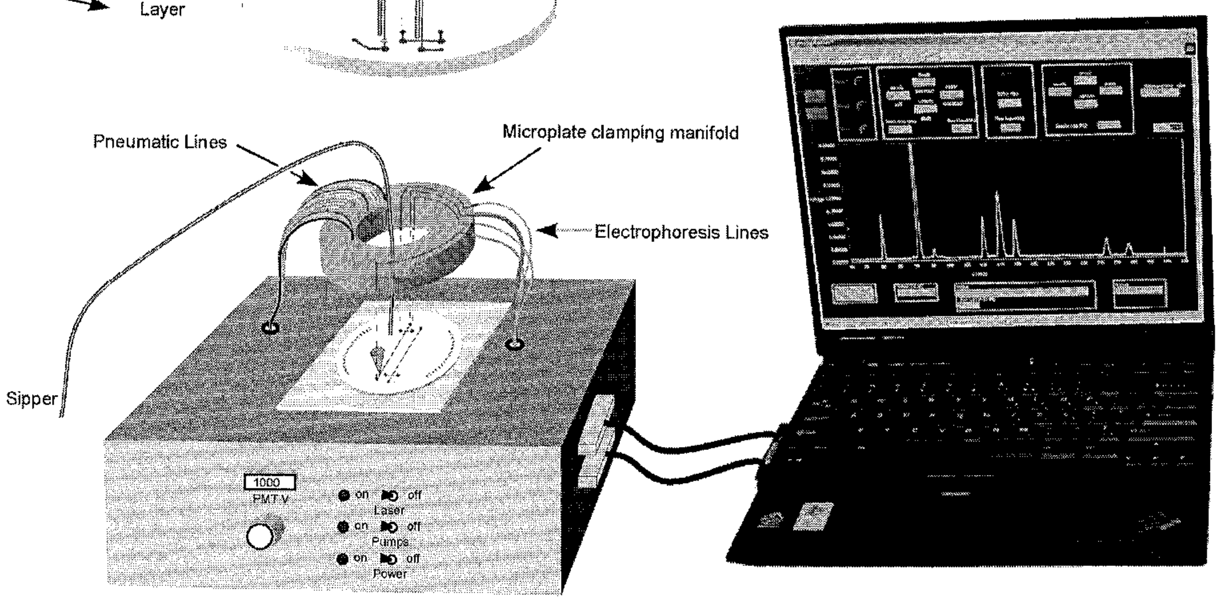




- Mars analog soil sample inoculated with E. coli cells
- 500˚C for 30 seconds
- UCSD (J. Bada, PI)

Portable Amino Acid Analysis Devices



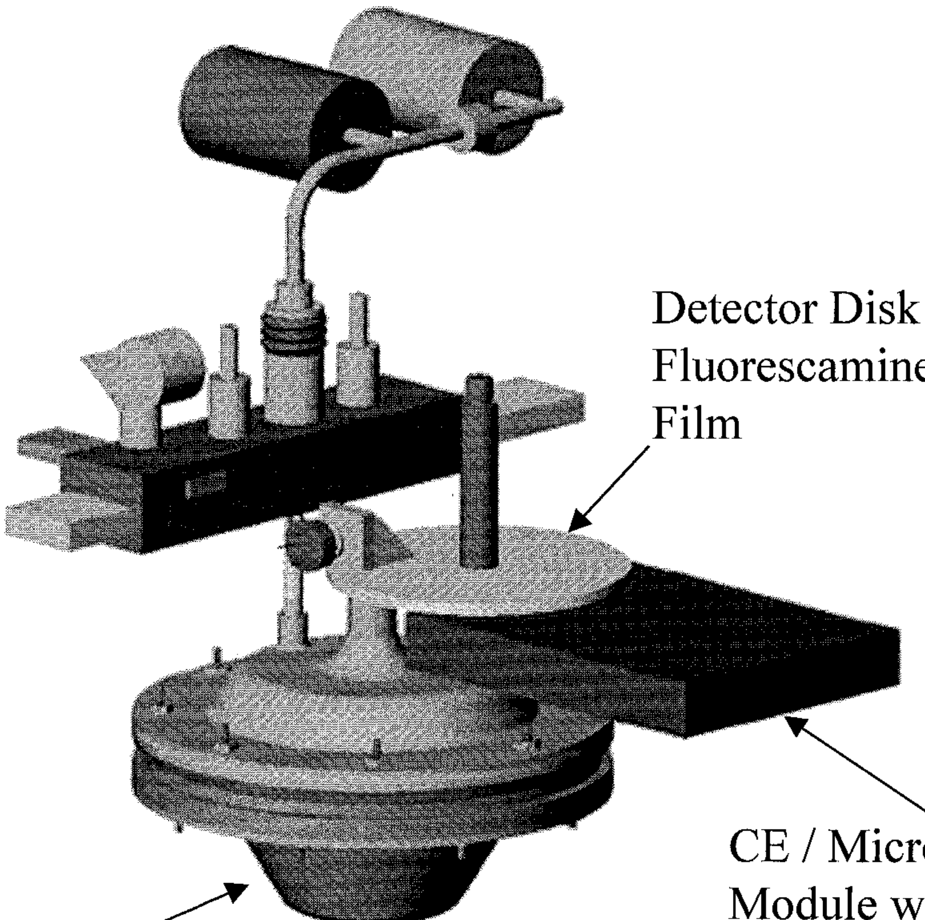


- 16 pneumatic lines for fluidic control
- Thermoelectric cooling
- Designed for either 404 nm (Fluorescamine) or 488 nm (FITC) diode laser
- Complete automated analysis for obtaining sample, labeling, diluting, and filling/flushing, CE channels for analysis

R. Mathies, UC Berkeley

Organic Analyzer for Life Detection

Systems are being developed that include highly complex sample preparation—

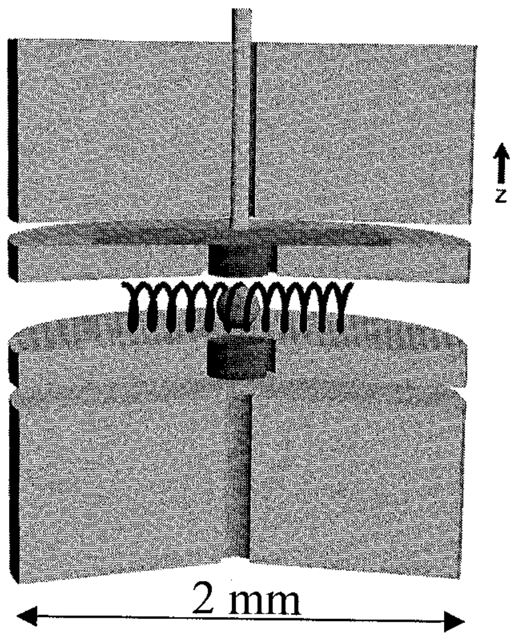


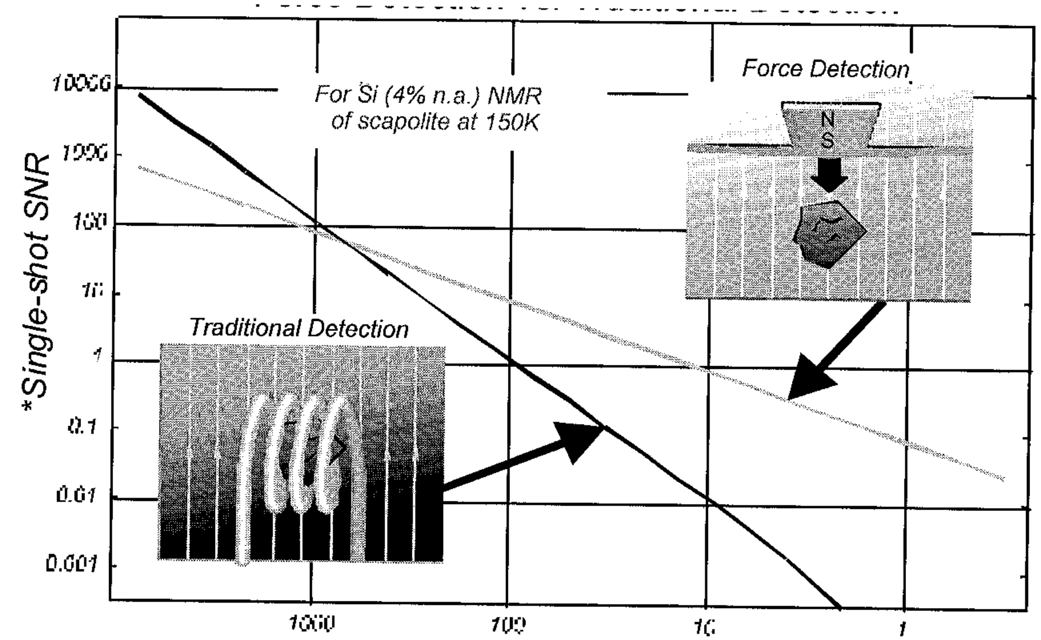
- Extracts, concentrates, fluorescently labels, and analyzes organic molecules
- Amino acids, amines, carboxylic acids, sugars, & nucleobases, including chirality
- 6 orders of magnitude more sensitive than Viking GCMS
- Martian soils, rocks, polar ice

JPL/UC San Diego/UC Berkeley

Force-Detection NMR

- 1 cm^3 volume, < 100 mW RF, several ppt accuracy for all isotopes with nuclear magnetic moments
- RF-induced change in magnetic moment sensed by movement of small central magnet suspended on beam (milli angstrom movement sensed by optical interferometry)

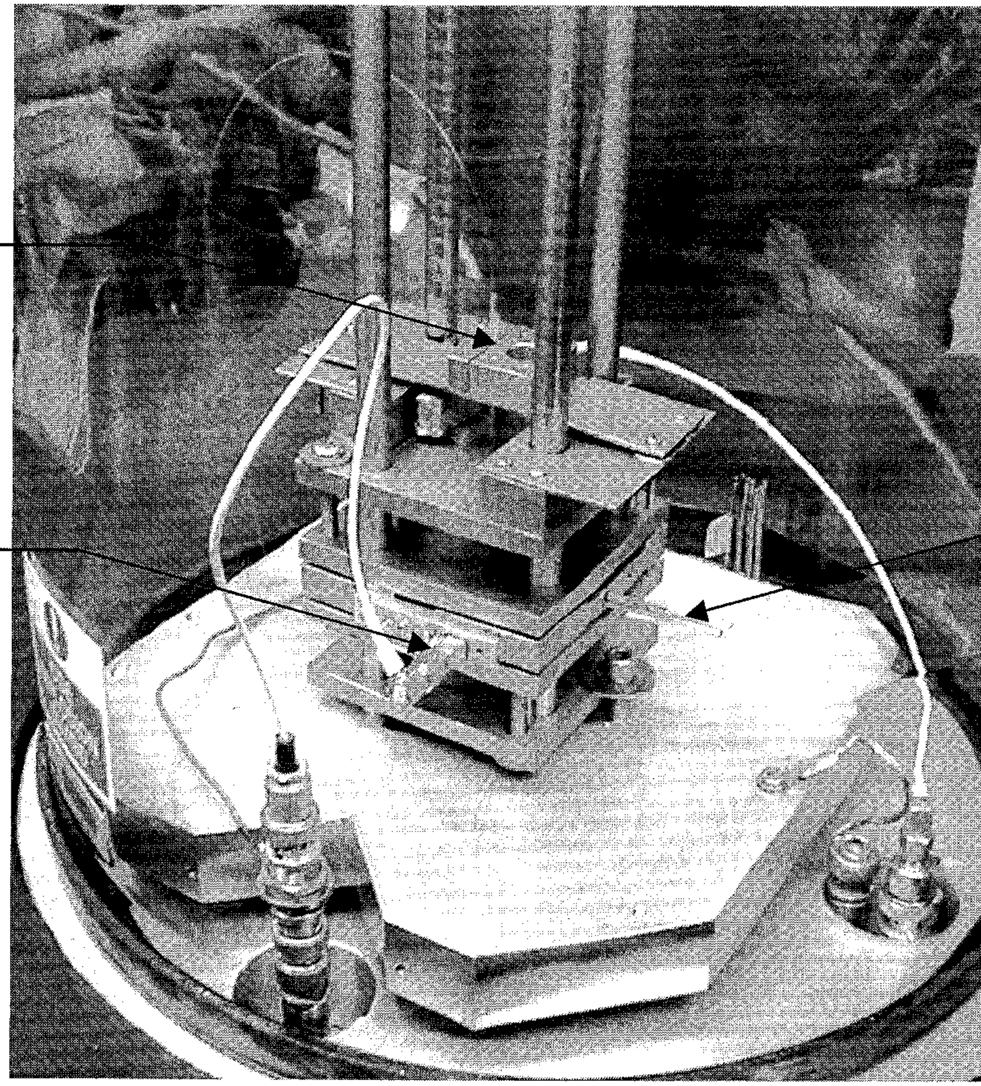




- Resolve chemically distinct sites and bonding environments from NMR line positions, amplitudes, relaxation times, & coupling constants
- Hydrocarbons in water, solid samples & mineral phases (especially good with light elements such as H, Li, B, C, N, F, Cl, and S), H_2S and hydrates, microbiological sensing (proteins, functional groups)

D. Weitkamp (CIT), T. George (JPL)

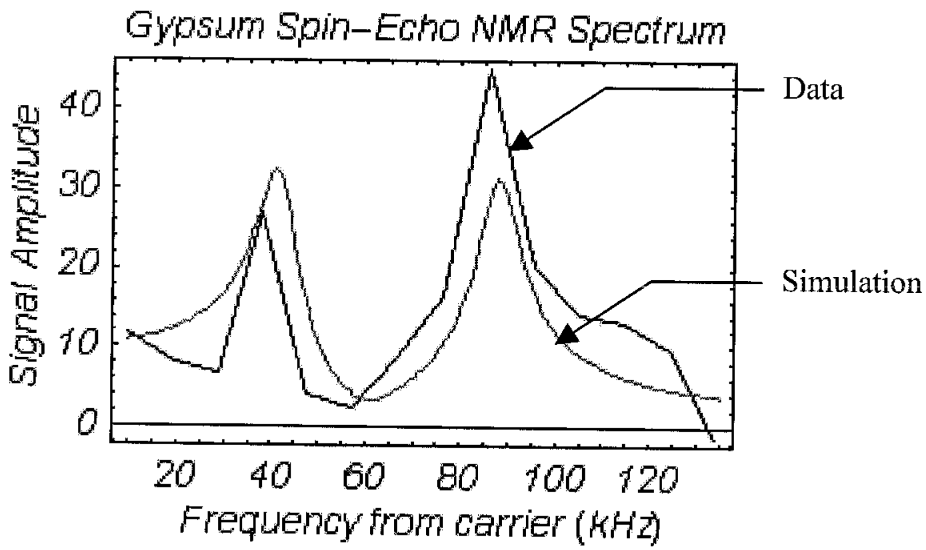
"Big Mac" laboratory test setup

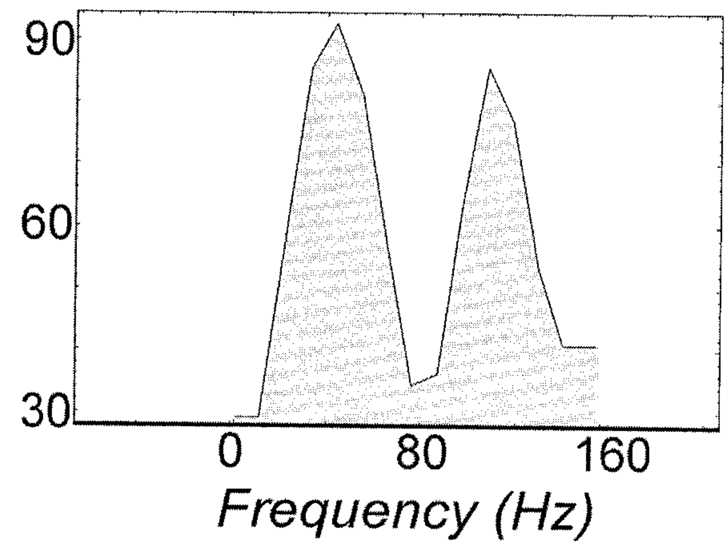


Proof-of-concept test setup for spectrometer which is 25x final size, tested in vacuum in a bell jar

Prof. D. Weitekamp (Caltech)
Thomas George (JPL)

FDNMR proof-of-concept spectra





- Using the "Bigmac" spectrometer, we have determined chemically specific material parameters that were previously not achievable via force detection techniques.

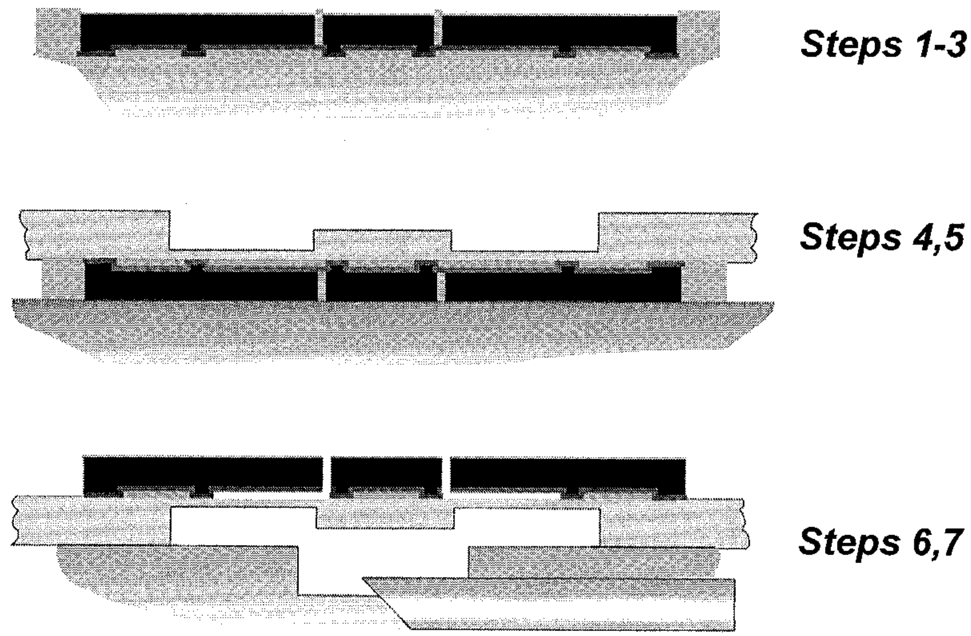
- Spectrum at left shows a splitting due to the intramolecular dipole-dipole coupling of hydrogens in the waters of hydration of a gypsum crystal.

- Spectrum at right shows a splitting, at much higher resolution, due to the ^{19}F-^{1}H through-bond, or "J", coupling in liquid fluoroacetonitrile (CF_2HCN).

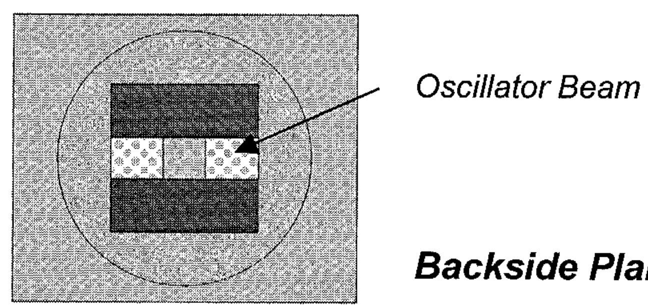
Prof. D. Weitekamp (Caltech)
Thomas George (JPL)

1-step plating fabrication process

1. Thermal oxidation and patterning for sacrificial layer.
2. Deposit Cr/Au (200Å/1000Å) plating seed layer and pattern photoresist mold.
3. Electroplate ring and detector magnets 10 μm thick.
4. Protect front side by wax-mounting to wafer.
5. Pattern back and create stress buttress and oscillator beam using deep RIE.
6. Remove sacrificial oxide (BOE).
7. Bond field magnet and fiber to back.



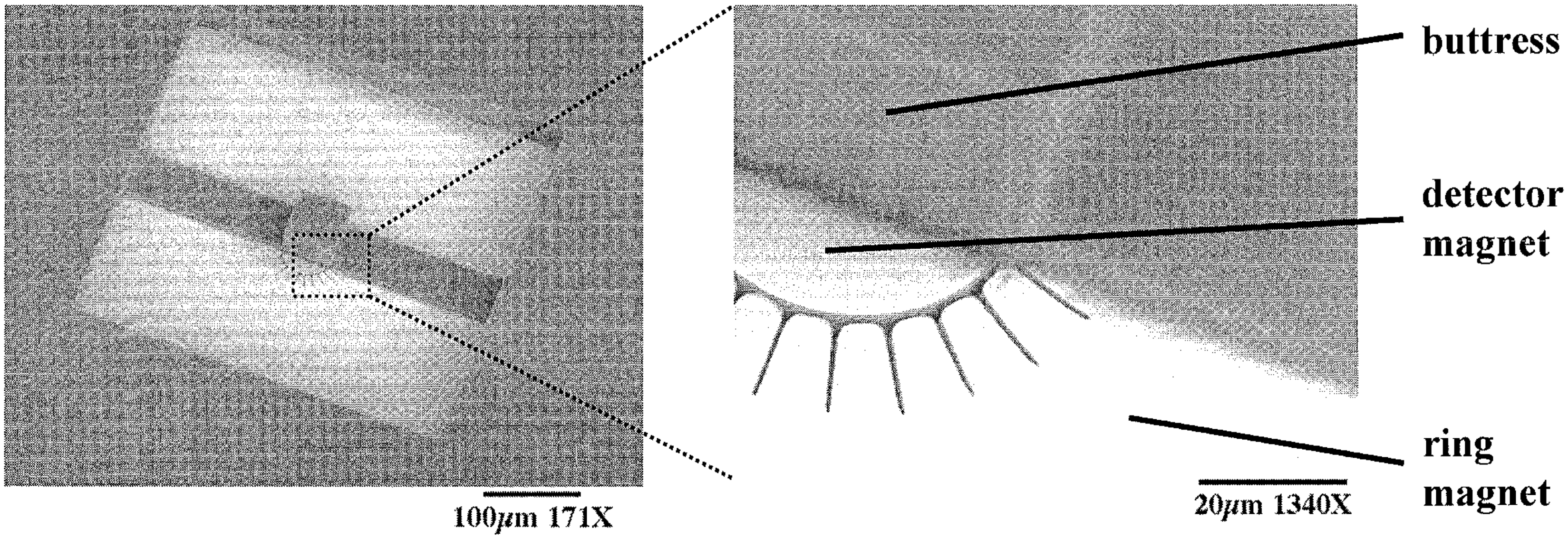
- silicon
- plated magnet
- oxide
- seed layer
- protect wafer
- field magnet
- photoresist
- fiber



Backside Plan View

Prof. D. Weitekamp (Caltech)
Thomas George (JPL)

Deep-RIE-defined beam and buttress with plated magnets

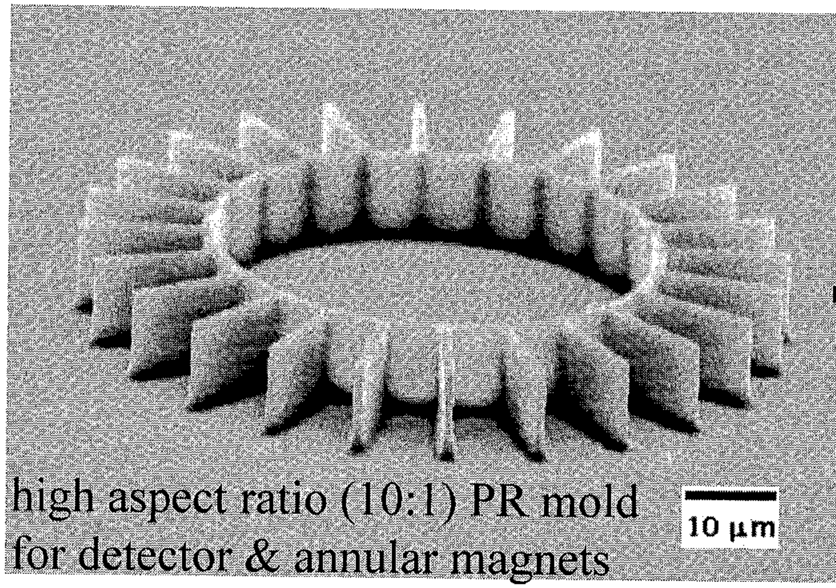


- **Deep RIE process used to define 5 μm-thick Si beam and stress buttress on backside of plated magnet array**
- **Detector/ring magnet gap is ~1 μm with slits for eddy-current reduction**
- **After release of PR and oxide sacrificial layers, magnets are still intact and not stress curled.**

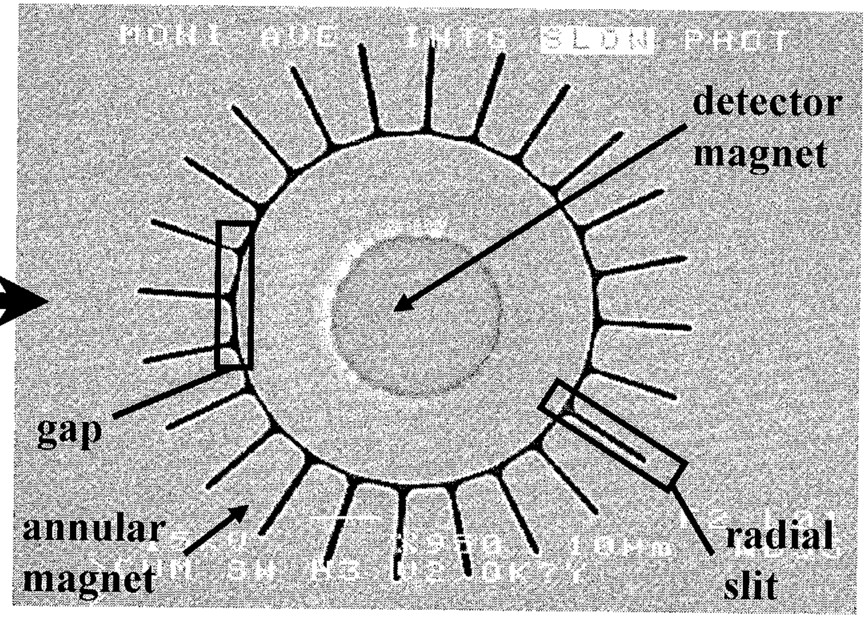
Prof. D. Weitekamp (Caltech)
Thomas George (JPL)

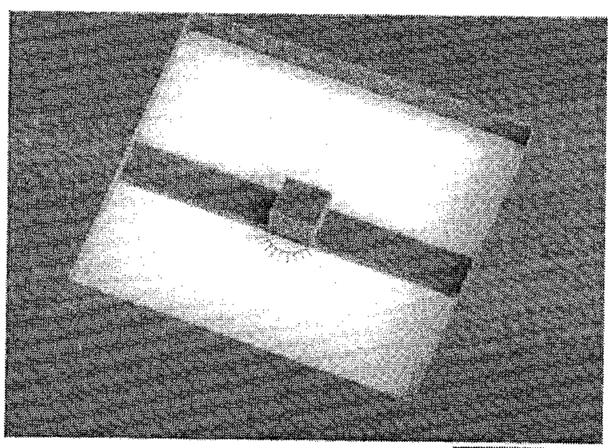
MEMS FD-NMR

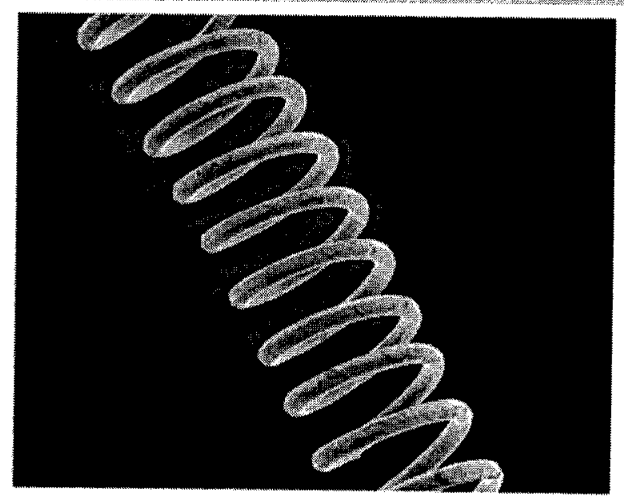
Nearing completion of microfabricated detectors for MEMS FD-NMR spectrometer—



high aspect ratio (10:1) PR mold for detector & annular magnets




100µm 171X



Acknowledgements

Allison Skelley, UCSD

J. Bada, UCSD

R. Mathies, UCB

F. Grunthaner, JPL

T. George, JPL

D. Weitekamp, Caltech

Dmitri Kossakovski

Greg Bearman, JPL

Rui Yang, JPL

Chris Webster, JPL

Thomas Pike, Imperial College, UK

Mark Anderson, JPL

Pan Conrad, JPL

Adrian Ponce, JPL

Jim Lambert, JPL


Questions?